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CARBAZOLYL NITRENIUM CATIONS: GENERATION AND REACTIONS

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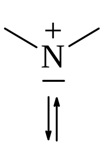
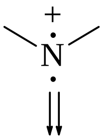
Abstract - Carbazolyl nitrenium cations were generated during the thermolysis and photolysis of 1-carbazol-9-yl-2,4,6-triphenylpyridinium (**Py$^+$-Cz**) tetrafluoroborate in 2,2,2-trifluoroethanol- and TFA - mesitylene mixtures. The thermolysis of **Py$^+$-Cz** in TFA-mesitylene mixture gave 9-mesitylcarbazole in good yield along with carbazole, non-symmetrical mesitylene dimer, 2,4,6-triphenylpyridine, and a small amount of 9-(3,5-dimethylbenzyl)carbazole, whereas the thermolysis in trifluoroethanol - mesitylene mixture gave 9-mesitylcarbazole as the main product along with carbazole and 2,4,6-triphenylpyridine. The product distributions lead to two major conclusions. First, photolysis and thermolysis of **Py$^+$-Cz** salt produce nitrenium ions that can be in singlet or triplet state dependant on the reaction conditions. Second, the carbazolyl nitrenium ion exhibits singlet state in the ground state.

INTRODUCTION

Nitrenium ions (R_2N^+) are reactive intermediates which contain a divalent, positively charged nitrogen atom and can possess either the singlet (S=0) (**I**) or triplet (S=1) (**II**) as the lowest energy configuration.[1] At the moment of reaction, the singlet or triplet nature of the nitrenium ions determines the type of products which will be formed; moreover, they may react in either the ground state or exited state. The singlet is capable of rearrangement,[2] addition to alkenes,[3] C-H insertion and electrophilic aromatic substitution[4,5] while the triplet usually abstracts hydrogen to form the parent amine.[6]



I



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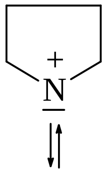


III

The parent nitrenium (H_2N^+) and simple alkyl derivatives (R_2N^+) are predicted to have a triplet ground state[7,8], and a photoionization study[8] shows the lowest singlet to be 3.0 kcal/mol above the triplet ground state of H_2N^+. The triplet-singlet energy gap is calculated to decrease with increasing substitution and indeed the nitrenium ion (**III**) is predicted to have a singlet ground state.[7,9] Further distortion of the C-N-C angles would stabilise the singlets.[10]

Arylnitrenium ions are expected to be more stable than alkyl substituted ions owing to the possible delocalization of the positive charge onto the ring. In general, benzene rings act as electron donors and stabilise the singlet relative to the triplet state.[9] The available *ab initio* calculation on phenyl nitrenium predicts the singlet is favoured by *ca.* 10 kcal/mol.[11] More recent semi-empirical calculations[12] show that nitrenium ions with aromatic substituents are ground-state singlets with substantial energy gaps. However, electron-withdrawing groups on the phenyl ring and sterically demanding substituents are both predicted to stabilize the triplet relative to the singlet state.[12]

In contrast to the other nitrenium ions, there is virtually nothing known about nitrenium ions derived from five-membered heteroaromatic nitrogen compounds e.g., pyrrole, indole, carbazole, imidazole, and triazoles. A great deal has been published on studies, both experimental and computational, of corresponding radicals and anions.[13] On the other hand, the only two papers about a possible generation and reactions of 4-(1,2,4-triazolyl) cation in the thermolysis of the 1-(1,2,4-triazol-4-yl)-2,4,6-trimethyl-pyridinium salt reported the formation of a variety of products, but none derived from attack of the free nitrenium ion. According to the authors, a possible explanation is a SET from trimethylpyridine to the nitrenium ion within the solvent cage.[14,15]

In the present article there are reported the preliminary studies on the generation and reactions of the nitrenium ions derived from carbazole. The experiments reported herein were undertaken with the aim of further characterising the generation of carbazolyl nitrenium ions. Of special interest is the behaviour of carbazolyl nitrenium ions and whether they exhibit the triple or singlet state in the ground state.

RESULTS AND DISCUSSION

The reaction of 9-aminocarbazole and 2,4,6-triphenylpyrylium tetrafluoroborate under the standard conditions produced 1-carbazol-9-yl-2,4,6-triphenylpyridinium tetrafluoroborate (**Py^+-Cz**). It was expected that the steric effect upon the phenyl groups at C-2 and C-6 of the pyridine ring and its elimination by N-N cleavage would provide an appropriate driving force for the desired generation of carbazolyl nitrenium ion.

A degassed solution of the pyridinium salt in a TFA - mesitylene or alternatively 2,2,2-trifluoroethanol - mesitylene mixture was heated or irradiated under the conditions described in Table 1, generating at least 5 compounds. After the work-up procedure, the products were isolated by preparative TLC chromatography, while yields were determined by gas chromatography.

Table 1: Thermolysis and Photolysis of 1-carbazol-9-yl-2,4,6-triphenylpyridinium tetrafluoroborate (**Py^+-Cz)** in TFA-mesitylene and 2,2,2-trifluoroethanol (TFE) -mesitylene solutions.

Py^+-Cz [mg]	TFA [mL]	Mesitylene [mL]	TFE [mL]	**1** [%]	**2** [%]	**3** [%]	**4** [%]	**5** [%]
100 [a)]	1.5	6.0	-	3	22	71	45	1
140 [a)]	3.0	7.0	-	5	26	64	40	2
100 [a)]	-	6.0	1.5	40	3	82	35	-
140 [a)]	-	6.0	3.0	37	6	74	39	-
100 [b)]	2.0	7.0	-	47	19	58	traces	-
140 [b)]	3.0	7.0	-	52	16	62	traces	-
100 [b)]	-	7.0	2.0	63	6	67	3	-
		benzene [mL]						
100 [b)]	1.5	7.0	-	54	-	70	-	-
140 [b)]	3.0	7.0	-	62	-	75	-	-
100 [b)]	-	7.0	3.0	58	-	70	-	-
140 [b)]	-	7.0	4.5	65	-	64	-	-

[a)] - thermolysis reaction; [b)] - photolysis reaction

The thermolysis in a TFA - mesitylene mixture at 162°C gave 9-mesitylcarbazole (**4**) in good yield along with carbazole (**1**), non-symmetrical mesitylene dimer (**2**), 2,4,6-triphenylpyridine (**3**), and 9-(3,5dimethyl-benzyl)carbazole (**5**), whereas the thermolysis in a trifluoroethanol-mesitylene mixture gave 9-mesitylcarbazole (**4**) as the main substitution product along with carbazole (**1**) and 2,4,6-triphenylpyridine (**3**); non-symmetrical mesitylene dimer (**2**) was detected in low yield.

The photolysis of the pyridinium salt in a TFA - mesitylene mixture gave 2,4,6-triphenylpyridine (**3**) and carbazole (**1**) in high yield along with the non-symmetrical mesitylene dimer (**2**); traces of 9-mesitylcarbazole (**4**) were detected. The photolysis of the pyridinium salt in a 2,2,2-trifluoroethanol - mesitylene mixture gave carbazole (**1**) as the main product along with the triphenylpyridine (**3**). Small amount of 9-mesitylcarbazole (**4**) was formed; the non-symmetrical mesitylene dimer (**2**) was detected in very low yield. The results are indicated in Table 1.

The formation of triphenylpyridine (**3**), to the exclusion of the salt from a radical cation of 2,4,6-triphenylpyridine, argues against initial homolysis of the pyridinium salt;[16] if the homolysis had occurred, a salt from radical cation of triphenylpyridine would be formed without contamination by triphenylpyridine. Moreover, the absence of 3,3',5,5'-tetramethyldiphenylethane makes a radical process unlikely.[17,18]

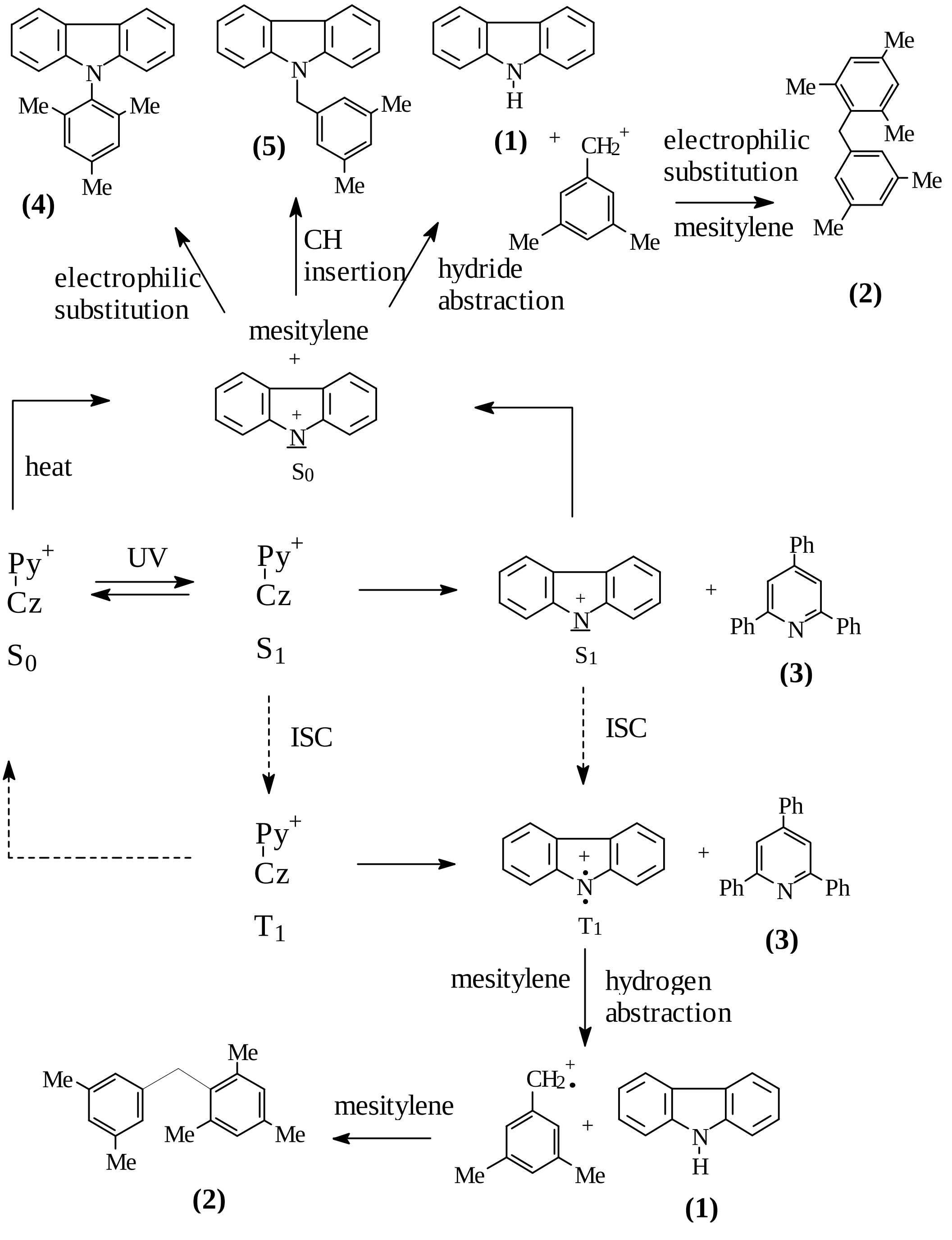
In contrast to the S_N2'reactions of 1-diphenylamino- and 1-carbazol-9-ylpyridinium cations with pyridine at 120°C, in which the nucleophile was capable of attacking only the *para* position of phenyl groups,[19] in the present case the mesitylene derived products, 9-mesitylcarbazole (**4**) and 9-(3,5-dimethylbenzyl)carbazole (**5**), arise here from the attack on mesitylene by an electrophilic intermediate, while the formation of the non-symmetrical mesitylene dimer (**2**) may be explained by invoking a mesitylene cation or radical cation intermediates.

As it is proposed in the reaction scheme (Figure 1), direct photolysis of 1-carbazol-9-yltriphenylpyridinium tetrafluoroborate forms the excited singlet of the pyridinium salt. The latter partitions between heterolytic decomposition of the pyridinium salt to give singlet nitrenium carbazolyl ions and intersystem crossing to give triplet pyridinium salt. The triplet undergoes heterolytic decomposition, giving triplet nitrenium carbazolyl ions. The difference in the product of photolysis and thermolysis may be attributed to the difference in the mechanism of reaction of the singlet and triplet nitrenium ions.

The singlet nitrenium ion either reacts with mesitylene to form the products like 9-mesitylcarbazole (**4**) and 9-(3,5-dimethylbenzyl)carbazole (**5**) or the mesitylene dimer by SET mechanism from the nitrenium ion. The formation of the non-symmetrical mesitylene dimer (**2**) may be explained by invoking a mesitylene radical cation intermediate.[16] The compound, 9-(3,5-dimethylbenzyl)carbazole (**5**), is the result of C-H insertion process of the singlet carbazolyl nitrenium ion to the methyl group in mesitylene. In order to prove the structure of the compound (**5**) as well as to compare it against the structure of the compound (**4**), it was prepared by alternative method (e.g., the direct reaction of α-chloromesitylene with carbazole under PTC conditions).

On the other hand, the triplet nitrenium ions either reacts by H atom transfer to form the parent amine, carbazole (**1**), or suffer intersystem crossing to singlet nitrenium ion. In both cases (e.g., photolysis in the presence of TFA or trifluoroethanol) 9-mesitylcarbazole (**4**) was formed in low yield, what indicates that intersystem crossing of triplet carbazolyl nitrenium ion to the singlet ground state is slower than H atom-transfer and formation of the parent amine, carbazole (**1**).

Both the singlet and triplet channels are possible in direct irradiation experiments, whereas only the singlet channel is operative in all the thermal experiments, and both the singlet and triplet products can be expected in photolytic reactions. Therefore, the simplest and most probable explanation is that the singlet is the ground state for the carbazolyl nitrenium cation. The relative yields of the products depend on the rate of intersystem crossing relative to heterolytic decomposition. The singlet ground state would agree with the analysis of our experiments as well as experiments and quantum-mechanical calculations on structurally similar arylnitrenium ions,[20,21]



Py⁺-Cz: 1-carbazol-9-yl-2,4,6-triphenylpyridinium tetrafluoroborate

Figure 1: Thermolysis and photolysis of 1-carbazol-9-yl-2,4,6-triphenylpyridinium tetrafluoroborate.

Thermal reactions are expected to initially generate the singlet nitrenium ion according to the view of mechanistic difference between thermolysis and photolysis. The yield of 9-mesitylcarbazole (**4**) in the thermolysis in the presence of TFA was higher than in the presence of trifluoroethanol. Possible reason for the lack of the formation of non-symmetrical mesitylene dimer (**2**) during the reaction in a trifluoroethanol - mesitylene mixture is that the hydride transfer is from trifluoroethanol rather faster than from mesitylene.

For the photolysis reaction, the yield of parent amine, carbazole (**1**), was higher in the presence of trifluoroethanol and it is likely that in the thermolysis experiments the yield of non-symmetrical mesitylene dimer (**2**) was much lower than for the reactions in a TFA - mesitylene mixtures

The photolysis of the pyridinium salt in benzene solutions produced only carbazole (**4**), and triphenylpyridine (**3**). Due to lower electron density on benzene than mesitylene ring, none of products arised from the attack of nitrenium ions on benzene was detected (Table 1).

CONCLUSIONS

Two major conclusions can derived from the present work. First, it is provided that photolysis and thermolysis of the 1-carbazol-9-ylpyridium salt produced nitrenium ions which can be in singlet or triplet state. The singlet carbazolyl nitrenium ion is produced by thermolysis of the pyridium salt, while the triplet state is generated by direct photolysis of the salt. The difference in the product distributions of photolysis and thermolysis reactions may be ascribe to different natures of the singlet and triplet nitrenium ions.

Second, the carbazolyl nitrenium ion exhibits singlet state in the ground state. Since the state of nitrenium ion controls its chemical reactivity, before quantitative spectroscopic and kinetic experiments (measurements) on nitrenium carbazolyl ions can be interpreted, the mechanism of photo- and thermal generation as well as subsequent chemical reactions must be well understood.

EXPERIMENTAL

IR spectra were recorded using a Bio-Rad FTS 165 spectrophotometer. ^{1}H-NMR spectra were taken with a Tesla 487 C instrument, TMS being used as an internal standard; the chemical shifts are expressed in δ-values downfield from TMS. MS spectra were recorded with a Hewlett-Packard GC/MS 5985 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyser. Melting points measured on a Boetius-PHMK 05 microscope plates are uncorrected. Preparative TLC was performed with Aluminiumoxid 60F 254 Typ E (5713) plates (Merck).

Dichloromethane, ethyl acetate, cyclohexane, acetone, toluene, and benzene were purified by standard methods before use. Mesitylene, trifluoroacetic acid and 2,2,2-trifluoroethanol were purified by distillation. The following compounds were reagent grade and used without further purification: carbazole (Fluka), 2,4,6-triphenylpyrylium tetrafluoroborate (Aldrich).

9-Nitrosocarbazole: A mixture of glacial acetic acid (100 mL), THF (100 mL), and carbazole (10 g, 60 mmol) was stirred at rt while sodium nitrite (8 g, 120 mmol) was added in small portions to the solution within 1 h. Stirring was continued for additional 3 h; the reaction flask was put a couple of times into hot water-bath to accelerate the reaction. Then THF was evaporated and water (100 mL) was added to precipitate a solid material. The recrystalisation of the solid from ethyl ether gave golden-yellow needles of 9-nitrosocarbazole (10 g, 85%). mp 80-82°C (lit.,[22] 80-82°C). *Anal*. Calcd for $C_{12}H_8N_2O$: C, 73.54; H, 4.14; N, 14.30. Found: C, 73.23; H, 3.98; N, 14.07.

9-Aminocarbazole: A mixture of glacial acetic acid (100 mL), THF (100 mL), and 9-nitrosocarbazole (5.0 g, 26 mmol) was stirred at rt while zinc dust (9 g, 138 mmol) was added in two portions to the solution within 30 min. Stirring was continued for additional 3 h. Then solid material was filtrated off and the solution was neutralised with 20% aqueous solution of potassium hydroxide. After evaporation of THF, the solid precipitated from the solution was filtered off and recrystalised from isooctane to afford 4.0 g (85%) of 9-aminocarbazole as long white needles. mp 147-9°C (lit.,[22] 151-152.5°C). *Anal*. Calcd for $C_{12}H_{1}0N_{2}$: C, 79.14; H, 5.52; N, 15.44. Found: C, 79.39; H, 5.40; N, 15.32.

1-Carbazol-9-yl-2,4,6-triphenylpyridinium tetrafluoroborate (Py-Cz$^+$): A solution of 9-amino-carbazole (0.42 g, 2.5 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate (0.92 g, 2.5 mmol) in ethanol (30 mL) was heated under reflux for 4 h. The product crystalized as yellow needles (1.2 g) while the solution was cooling down. The recrystalisation from ethanol gave 1-carbazol-9-yl-2,4,6-triphenyl-pyridinium tetrafluoroborate as yellow plates (0.97 g, 70%). mp 204-206°C (lit.,[19] 210-212°C). *Anal*. Calcd for $C_{35}H_{25}N_2BF_4$: C, 75.03; H, 4.51; N, 5.02. Found: C, 75.30; H, 4.67; N, 4.71.

Thermolysis of 1-carbazol-9-yl-2,4,6-triphenylpyridinium tetrafluoroborate (Py-Cz$^+$): Thermolysis of 1-carbazol-9-yl-2,4,6-triphenylpyridinium tetrafluoroborate was carried out in a sealed tube at 162°C. Detail conditions are given in Table 1. After the reaction, 10% solution of potassium carbonate was added to the mixture till the pH of the solution exceeded 7. The organic layer was extracted with ethyl acetate. After that the products were isolated by preparative TLC while yields were determined by GC/MS analysis. Carbazole and 2,4,6-triphenylpyridine were identified by comparison with original samples, whereas the structures of following compounds were confirmed by spectroscopic methods.

9-Mesitylcarbazole (4): mp 152-154°C; ^{1}H-NMR ($CDCl_3$): 1.81 (s, 6H, 2x($-CH_3$)), 2.41(s, 3H, $-CH_3$), 6.89-7.40 (m, 6H, aromatic rings), 8.11-8.22 ppm (m, 2H, aromatic rings of carbazole); IR (KBr): 3050(w), 3016w), 2918(m), 2852(m), 1626(m), 1594(m), 1495(s), 1476(s), 1451(s), 1314(s), 1234(s), 751(s), 721(s) cm^{-1}. MS (m/z) 286 (22)(M+1) 285 (100)(M$^+$). *Anal.* Calcd for $C_{21}H_{19}N$: C, 88.40; H, 6.74; N, 4.91. Found: C, 88.32; H, 6.99; N, 4.60.

2-(3,5-Dimethylbenzyl)-1,3,5-trimethylbenzene (non-symmetrical mesitylene dimer) (2): mp 69-71°C (lit.,[23] 67-68°C). ^{1}H-NMR ($CDCl_3$): 2.20 (s, 6H, 2x($-CH_3$), 3',5'-), 2.23 (s, 6H, 2x($-CH_3$), 2,6-), 2.29 (S, 3H, $-CH_3$, 4-), 3.93 (s, 2H, $-CH_2-$), 6.63 (s, 2H, *ortho*-aromatic ring), 6.73 ppm (s, 1H, *para*-aromatic ring), 6.88 (s, 2H, *meta*-aromatic ring); IR (KBr): 3020(m), 2975(s), 2915(m), 2880(m), 1609(m), 1505(s), 1458(s), 1385(m), 1020(m), 880(s), 820(s), 815(m) cm^{-1}. MS (m/z): 239(17) (M+1), 238(86) (M$^+$), 223(57) (M-(CH_3)), 208(12) (M-2x(CH_3)), 193(14) (M-3x(CH_3)), 132(65) (mesitylyl-CH$^+$),119(26) (mesitylyl$^+$), 91(11) (phenyl-CH$^+$). The structure of the compounds was confirmed by the comparison against the physical and spectra data for the symmetrical mesitylene dimer (2,4,6,2',4',6'-hexamethyl-biphenyl).[17]

Photolysis of 1-carbazol-9-yl-2,4,6-triphenylpyridinium tetrafluoroborate (Py-Cz$^+$): Photolysis of 1-carbazol-9-yl-2,4,6-triphenylpyridinium tetrafluoroborate was conducted externally in a quartz tube (25 x 2 cm) with a high pressure mercury lamp (400 W) after purging with dry argon for 15 min. During the reaction the solution was stirred with a small magnetic bar. Details conditions are given in Table 1. Analysis and characterisation of the products were performed as for the thermal reactions.

9-(3,5-Dimethylbenzyl)carbazole (5): A solution of benzoyl peroxide (0.12 g, 0.50 mmol), freshly distilled sulfuryl chloride (5 mL, 50 mmol), and mesitylene (35 mL, 250 mmol) was stirred at 100°C for

1 h. After cooling down traces of sulfuryl chloride were evaporated under reduced pressure to afford 1.4 M solution (35 mL) of α-chloromesitylene in mesitylene. The concentration of the solution was determined by means of gas chromatography. In the next step, the solution of the chloromesitylene (7 mL, 10 mmol) was added dropwise within 1 h to a solution of carbazole (1.67 g, 10 mmol) in a mixture of water (10 mL), NaOH (10 g), heptane (40 mL), and tetrabutylammonium chloride (0.2 g) at 90^{o}C. The reaction was continued for additional 2 h while all the time the mixture was vigorously stirred. Then aqueous phase was separated and washed with methylene chloride (2 x 25 mL). The extract was combined with the organic phase and solvents were evaporated under reduced pressure to give a heavy oil. Recrystallisation from heptane affords 9-(2,4-dimethylbenzyl)carbazole as long white needles (2.45 g, 86%); mp 119-121^{o}C. ^{1}H-NMR ($CDCl_3$): (s, 6H, 2x(-CH_3)), 5.41 (s, 2H, -CH_2-), 6.77 (s, 2H, ortho-aromatic ring), 6.84 (s, 1H, *para*-aromatic ring), 7.12-7.45 (m, 6H, aromatic rings of carbazole), 8.06-8.14 ppm (m, 2H, aromatic rings of carbazole). IR (KBr): 3050(m), 3019(m), 2915((m), 2857(m), 1627(m), 1595(m), 1484(s), 1459(s), 1324(s), 1211(s), 750(s), 722(s) cm^{-1}; MS (m/z): 286(20) (M+1), 285(70) (M^+), 119(100) (mesitylyl$^+$). *Anal.* Calcd for $C_{21}H_{19}N$: C, 88.40; H, 6.72; N, 4.94. Found: C, 88.45; H, 6.84; N, 4.70.

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