Synthesis and Electronic Spectroscopy of Bromocarbazoles. Direct Bromination of *N*- and *C*-Substituted Carbazoles by *N*-Bromosuccinimide or a *N*-Bromosuccinimide/Silica Gel System

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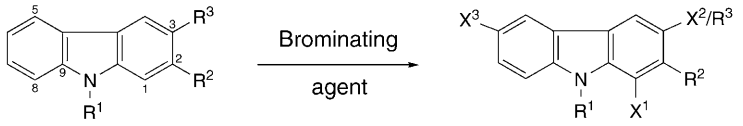
The preparation, isolation and characterization by elemental analysis and ^{1}H-NMR, ^{13}C-NMR, and MS data of the bromo derivatives of *N*-substituted carbazoles, *i.e.*, of 9-methyl-9*H*-carbazole (**1**), 9-phenyl-9*H*-carbazole (**2**), 9-benzyl-9*H*-carbazole (**3**), 2-methoxy-9-methyl-9*H*-carbazole (**4**), and of *C*-substituted carbazoles, *i.e.*, of 2-(acetyloxy)-9*H*-carbazole (**5**) and 3-nitro-9*H*-carbazole (**6**), are reported, in part for the first time. As brominating reagents, *N*-bromosuccinimide (NBS) or NBS/silica gel in CH_2Cl_2, NBS in AcOH, $KBrO_3$/KBr in EtOH doped with a catalytic amount of H_2SO_4, or $KBrO_3$/KBr in AcOH were employed, and their uses were compared. Semi-empirical PM3 calculations were performed to predict the reactivity of the *N*-substituted and *C*-substituted carbazoles and of their bromo derivatives and found to verify the experimental results. The UV-absorption and fluorescence and phosphorescence emission spectra of the bromocarbazole derivatives in MeCN solution at 298 K and in a solid matrix at 77 K were compared with those of the corresponding carbazoles **1**–**6**. The dynamic properties of the lowest excited singlet and triplet states (τ_f, τ_p, ϕ_f, and ϕ_p) were measured under the same experimental conditions. The intramolecular spin–orbital-coupling effect of the Br-atom and NO_2 group on the spectroscopic data, photophysical parameters, and on the photo reactivity were also briefly analyzed.

Introduction. – As part of our ongoing program on the photochemistry of azacarbazoles [1–6], carbazoles [7–8], *N*-acyl- and *N*-alkylcarbazoles [9–11], and nitrocarbazoles [12] and especially on the photoinduced electron-transfer process in which they can be involved [12b], we decided to go on with the study of the photophysical properties of bromo derivatives of several *N*- and *C*-substituted carbazoles. Furthermore, we are interested in the photoinduced heterolytic cleavage of the C–Br bond in polycyclic and heterocyclic bromo-substituted aromatic compounds. In these cases, the aryl (or heteroaryl) cation formed from the triplet excited state can react with different nucleophiles, such as olefines, arenes, or nucleophilic solvents forming new C–C or C–heteroatom bonds in a clean and one-pot photoreaction step [13]. Thus, to begin with, we now report the synthesis, characterization, and electronic spectra of several *N*- and *C*-substituted bromocarbazoles prepared by direct bromination of 9-methyl-9*H*-carbazole (**1**), 9-phenyl-9*H*-carbazole (**2**), and for the first time, of 9-benzyl-9*H*-carbazole (**3**), 2-methoxy-9-methyl-9*H*-carbazole (**4**), 2-(acetyloxy)-9*H*-carbazole (**5**), and 3-nitro-9*H*-carbazole (**6**) (see **3a**,**b**, **4a**–**c**, **5a**–**c**, and **6a** in *Scheme 1*).

Traditionally, the direct bromination reaction of arenes and heteroarenes, were carried out with Br_2 in the presence of a catalyst, most often iron. Ferric chloride and other

Scheme 1



	R^1	R^2	R^3
1	Me	H	H
2	Ph	H	H
3	$PhCH_2$	H	H
4	Me	MeO	H
5	H	AcO	H
6	H	H	NO_2

	X^1	X^2/R^3	X^3	R^1	R^2
1a	Br	H	H	Me	H
b	H	Br	H	Me	H
c	Br	H	Br	Me	H
d	H	Br	Br	Me	H
2a	H	Br	H	Ph	H
b	H	Br	Br	Ph	H
3a	H	Br	H	$PhCH_2$	H
b	H	Br	Br	$PhCH_2$	H
4a	H	Br	H	Me	MeO
b	H	Br	Br	Me	MeO
c	Br	Br	Br	Me	MeO
5a	H	Br	H	H	AcO
b	H	H	Br	H	AcO
c	H	Br	Br	H	AcO
6a	H	NO_2	Br	H	H

Lewis acids are often directly used as catalysts, as is I_2 [14]. Bromination of the aromatic moiety can be achieved in the presence of thallium(III) acetate which induces a high regioselectivity *para* to an *ortho–para*-directing group [15]. For activated aromatic compounds, including amines, phenols, naphthalene, and polyalkylbenzenes, no catalyst is needed. Indeed, the bromination is so rapid that it is carried out with a dilute solution of Br_2 in H_2O at room temperature. But even under these experimental conditions, dibromination and tribromination take place when the aromatic moiety is activated for electrophilic aromatic substitution. Thus, the chemical yield of monobromo derivatives is considerably diminished. A mixture of KBr and $KBrO_3$ in EtOH in the presence of catalytic amounts of sulfuric acid has been used as a direct brominating agent, but regioselectivity is difficult to improve [16]. Other brominating methods have been used, among them HOBr and *N*-bromoamides, such as *N*-bromosuccinimide and tetraalkylammonium tribromide [17]. In general, these reactions are acid-catalyzed. Dibromoisocyanuric acid in the presence of sulfuric acid is a very good brominating agent for substrates with strongly deactivating substituents [18]. Also, a mixture of KBr and KNO_3 in AcOH at 80° is used as a brominating agent [19]. Nevertheless, bromo and nitro derivatives are obtained in the reaction mixture, and when the temperature is raised, only the nitration reaction takes place. As a brominating agent, also HBr in dimethylsulfoxide has been employed, but fails as a general brominating agent because the oxidation power of the reaction mixture is important, and alkyl or alkenyl substituent groups present in the aromatic compound are easily oxidized [20]. These brominating methods are less commonly used because aromatic compounds with acid-sensitive functions or oxidizeable substituent groups such as esters, amides, acyloxy derivatives, amines, and alkyl compounds are easily hydrolyzed, protonated and/or oxidized under the above mentioned experimental conditions.

The synthesis of 3-bromo-9-methyl-9*H*-carbazole and of 3,6-dibromo-9-methyl-9*H*-carbazole has been described a long time ago [16]. This previously described bromination reaction of 9-methyl-9*H*-carbazole (**1**) with Br_2 in AcOH at room temperature provided 3,6-dibromo-9-methyl-9*H*-carbazole (**1d**), after recrystallization from AcOH. When $KBrO_3$/KBr in AcOH was used as the brominating agent, a mixture of 3-bromo- (**1b**) and 3,6-dibromo-9-methyl-9*H*-carbazole (**1d**) was obtained. These compounds were characterized by their melting point and ^{1}H-NMR and IR spectra but no UV-absorption and emission data were published [21]. Although *Ambrose et al.* [21] pointed out that the purity and the structure of obtained **1d** was confirmed by ^{1}H-NMR spectroscopy, no spectroscopic data were reported. The 3,6-dibromo-9-phenyl-9*H*-carbazole (**2b**) was prepared from 9-phenyl-9*H*-carbazole (**2**) with 2 equiv. of Br_2 in AcOH at room temperature and characterized only by its melting point and elemental analysis [21].

To the best of our knowledge, the direct bromination of 9-benzyl-9*H*-carbazole (**3**), 2-methoxy-9-methyl-9*H*-carbazole (**4**), 2-(acetyloxy)-9*H*-carbazole (**5**), and 3-nitro-9*H*-carbazole (**6**) has not been described. Furthermore, several bromo derivatives of these carbazoles and some of carbazoles **1** and **2** are not known. Recently, we have described *N*-chlorosuccinimide [22] and *N*-iodosuccinimide [23] in CH_2Cl_2 or $CHCl_3$ as successful, convenient, and mild chlorinating and iodinating agents providing mono-, di-, and polychloro and -iodo compounds, respectively, depending on the stoichiometry used. *Smith et al.* [24] have shown that *N*-bromosuccinimide (NBS) in $CHCl_3$ is a versatile brominating agent for heterocyclic compounds, and in the case of carbazole, mono-, di-, tri-, or tetrabromo derivatives were obtained depending on the stoichiometry used.

In the present paper, we describe the preparation, isolation, and characterization of several bromocarbazoles obtained from the *N*-substituted and *C*-substituted carbazoles **1**–**6** (*Scheme 1*) by direct bromination with two types of brominating agents, *i.e.*, $KBrO_3$/KBr in the presence of the acid catalysts sulfuric acid or AcOH, and NBS in CH_2Cl_2 in the presence or absence of silica gel and in AcOH. These brominating systems are mild reagents for the selective preparation of *N*-substituted and *C*-substituted mono- and dibromocarbazoles, providing for the first time the bromocarbazoles **3a**,**b**, **4a**–**c**, **5a**–**c**, and **6a** (see *Scheme 1*). Additionally, atomic-charge densities were calculated and used to discuss the reactivity of carbazoles **1**–**6**. Finally, the UV-absorption and fluorescence and phosphorescence emission data of the bromocarbazole derivatives were compared with those of the corresponding carbazoles **1**–**6**, and the dynamic properties of the lowest excited singlet and triplet states (τ_f, τ_p, ϕ_f, and ϕ_p) were measured. The intramolecular heavy-atom effects of the Br-atom and the NO_2 group on the spectroscopic and photophysical properties are discussed briefly.

Results and Discussion. – *Bromination of Carbazoles.* To investigate the bromination of the carbazoles **1**–**6**, we proceeded systematically and comparatively using different brominating reagents. Thus, five different methods (*i*)–(*v*) were employed: (*i*) NBS in CH_2Cl_2, (*ii*) NBS in CH_2Cl_2 in the presence of SiO_2, (*iii*) NBS in AcOH, (*iv*) $KBrO_3$/KBr in MeOH in the presence of catalytic amounts of conc. sulfuric acid and (*v*) $KBrO_3$/KBr in AcOH as solvent and acid catalyst. These brominations were carried out at room temperature to get the bromocarbazole derivatives in high yield.

Thus, 9-methyl-9*H*-carbazole (**1**) was treated according to the general procedure described in *Exper. Part* with 1–2 equiv. of NBS or NBS/SiO_2 in CH_2Cl_2 or NBS in AcOH. The yields of the bromocarbazole derivatives **1a**–**d** were determined by GC after an appropriate time, and the results are presented in *Table 1*.

Table 1. *Bromination of 9-Methyl-9*H*-carbazole* (**1**) *by Different Methods*

Entry	Method[a])	Carbazole **1**/BA[b]) [molar ratio]	Conversion [%]	Products [% yield][c])			
				1a	**1b**	**1c**	**1d**
1	(*i*)	1:1	92.1	0.7	91.4	–	–
2	(*ii*)	1:1	94.7	1.9	79.4	–	13.4
3	(*iii*)	1:1	100	1.5	67.7	–	30.8
4	(*iv*)	1:1	100	–	50.1	–	49.9
5	(*v*)	1:1	100	–	57.8	3.6	32.8
6	(*i*)	1:2	100	0.5	29.3	1.0	69.2
7	(*ii*)	1:2	100	–	–	–	92.3
8	(*iii*)	1:2	100	–	–	3.1	96.9
9	(*iv*)	1:2	100	–	7.1	1.9	90.5
10	(*v*)	1:2	100	–	–	–	100

[a]) Reaction time: 20 min; all experiments were carried out at room temperature. (*i*) NBS/CH_2Cl_2, (*ii*) NBS/CH_2Cl_2/SiO_2, (*iii*) NBS/AcOH, (*iv*) KBr/$KBrO_3$/MeOH/H_2SO_4 (cat.), and (*v*) KBr/$KBrO_3$/AcOH. [b]) BA = brominating agent. [c]) Quantitative GC (*Ultra 2*) analysis.

When 1 equiv. of NBS in CH_2Cl_2 was used, 3-bromocarbazole **1b** was obtained in 91% yield besides traces of 1-bromocarbazole **1a** (*Table 1, Entry 1*). With 1 equiv. of NBS in the presence of an acid catalyst such as SiO_2 or AcOH, 3-bromocarbazole **1b** was still the main product but 3,6-dibromocarbazole **1d** was formed in a significant amount (*Entries 2* and *3*, resp.), besides traces of **1a**. These results can be rationalized by the presence of acetyl hypobromite (MeCOOBr) as attacking agent when AcOH is the acid catalyst, this brominating agent being formed according to the equilibrium reaction shown in *Scheme 2*. When silica gel is used as a catalyst agent, one possible attacking agent present in the reaction mixture is hypobromite acid (HBrO). Thus, comparing the results of *Entries 1–3* led us to conclude that the release of the electrophile species, the bromonium ion (Br^+), from NBS in CH_2Cl_2 under neutral conditions is slower than the formation of MeCOOBr or HBrO under acidic conditions. Therefore, the reaction with NBS (1 equiv.) is regioselective under neutral conditions yielding the monobromo product **1b**. Under acidic conditions, the regioselectivity decreases with concomitant increase of dibromination.

When 9-methyl-9*H*-carbazole (**1**) was treated with 1 equiv. of the classical brominating agent, a mixture of $KBrO_3$/KBr in the presence of a catalytic amount of a min-

Scheme 2

eral acid (conc. sulfuric acid) in MeOH at 25°, 3-bromocarbazole **1b** and 3,6-dibromocarbazole **1d** were formed in a 1:1 molar ratio (*Table 1*, *Entry 4*). A similar trend was observed in the classical bromination of **1** in the presence of AcOH, **1b** and **1d** being formed in a 2:1 molar ratio (*Entry 5*). These results confirm our conclusions about the loose of regioselectivity on monobromination of **1** under acidic conditions due to the possible presence of the attacking agents MeCOOBr or HBrO in the reaction mixture. However, when the classical brominating method is used, other brominating species derived from hypobromous acid such as H_2BrO^+, Br_2O, or Br^+ might be present which are indistinguishable at the present time. Additionally, the brominating species H_2BrO^+ may be operative in the bromination of **1** in the presence of a catalytic amount of conc. sulfuric acid ($H_0 = -1.87$).

Treatment of 9-methyl-9*H*-carbazole (**1**) with 2 equiv. of NBS under neutral conditions yielded compounds **1b** and **1d** in a 3:7 molar ratio (*Table 1*, *Entry 6*). In the same reaction under acidic conditions (SiO_2 or AcOH), 3,6-dibromocarbazole **1d** was formed in >90% yield (*Entries 7* and *8*). Similar results were obtained with the classical brominating agents $KBr/KBrO_3/MeOH/H_2SO_4$ (cat.) or $KBr/KBrO_3$/AcOH, **1d** being again the main product (*Entries 9* and *10*). Thus, regioselective dibromination of **1** can be achieved in an easy and clean way when acidic conditions are used.

The 9-phenyl-9*H*-carbazole (**2**) and 9-benzyl-9*H*-carbazole (**3**) are less reactive than 9-methyl-9*H*-carbazole (**1**). Thus, the bromination with NBS (1 equiv.) in CH_2Cl_2 under neutral or acidic conditions required longer periods of time. Monobromination of **2** and **3** produced the expected products, *i.e.*, 3-bromocarbazoles **2a** and **3a**, respectively, in good yields (*Entries 1–3* in *Tables 2* and *3*). In some of these reactions, significant amounts of the corresponding 3,6-dibromocarbazoles **2b** or **3b** were also obtained (*Entry 2* in *Table 2* and *Entries 1* and *2* in *Table 3*). Nevertheless, the monobromo compounds **2a** and **3a** were obtained in high yield with NBS (1 equiv.) under neutral conditions. The bromination of **2** and **3** with 2 equiv. of NBS under neutral and acidic conditions gave the 3,6-dibromocarbazoles **2b** and **3b**, respectively, in fairly good yield, besides a significant amount of the monobromo compounds **2a** and **3a**, except for one case (*Entries 6–8* in *Tables 2* and *3*). Thus dibromination of **2** and **3** with NBS is best conducted under neutral conditions. In particular, **3b** was obtained in almost 100% yield under neutral conditions. The bromination of **2** and **3** with 1 equiv. of $KBr/KBrO_3$ in MeOH under acidic conditions produced the 3-bromocarbazoles **2a** and **3a** besides the 3,6-dibromocarbazoles **2b** and **3b**, respectively (*Entries 4* and *5* in *Tables 2* and *3*), monobromination being favored in the case of $KBr/KBrO_3$ in the presence of a catalytic amount of conc. sulfuric acid. With 2 equiv. of the classical brominating agent, dibromination of **2** and **3** took place preferentially, yielding **2b** and **3b** as the main product, respectively, except for one case, besides **2a** and **3a** in a significant amount, except for one case (*Entries 9* and *10* in *Tables 2* and *3*).

It is noteworthy to mention that in the bromination reaction of 9-methyl-9*H*-carbazole (**1**), 1-bromocarbazole **1a** and 1,6-dibromocarbazole **1c** were formed in very low yield (<1%) while, in the bromination of 9-phenyl- (**2**) and 9-benzyl-9*H*-carbazole (**3**), neither 1-bromo- nor 1,6-dibromocarbazoles were detected in the reaction mixtures. Comparing these results with those obtained in the chlorination [22b] and iodination [23b] of *N*-substituted carbazoles, we conclude that the reactivity of the incoming electrophile Br^+ at the *ortho*-position of the carbazole moiety is dramatically dimin-

Table 2. *Bromination of 9-Phenyl-9*H*-carbazole* (**2**) *by Different Methods*

Entry	Method[a])	Carbazole **2**/BA[b]) [molar ratio]	Conversion [%]	Products [% yield][c])	
				2a	**2b**
1	(*i*)	1:1	95.5	91.5	–
2	(*ii*)	1:1	96.3	89.6	6.8
3	(*iii*)	1:1	85.0	83.7	–
4	(*iv*)	1:1	89.0	86.2	–
5	(*v*)	1:1	100	79.0	18.0
6	(*i*)	1:2	100	12.5	87.5
7	(*ii*)	1:2	100	25.1	74.9
8	(*iii*)	1:2	100	27.1	72.9
9	(*iv*)	1:2	100	21.4	78.6
10	(*v*)	1:2	100	59.8	38.4

[a]) Reaction time: 60 min; all experiments were carried out at room temperature. (*i*) NBS/CH_2Cl_2, (*ii*) NBS/CH_2Cl_2/SiO_2, (*iii*) NBS/AcOH, (*iv*) KBr/$KBrO_3$/MeOH/H_2SO_4 (cat.), and (*v*) KBr/$KBrO_3$/AcOH. [b]) BA = brominating agent. [c]) Quantitative GC (*Ultra 2*) analysis.

Table 3. *Bromination of 9-Benzyl-9*H*-carbazole* (**2**) *by Different Methods*

Entry	Method[a])	Carbazole **3**/BA[b]) [molar ratio]	Conversion [%]	Products [% yield][c])	
				3a	**3b**
1	(*i*)	1:1	90.0	84.7	5.2
2	(*ii*)	1:1	82.3	78.8	3.7
3	(*iii*)	1:1	82.0	79.6	–
4	(*iv*)	1:1	100	85.9	13.0
5	(*v*)	1:1	65.0	4.0	60.5
6	(*i*)	1:2	100	–	98.5
7	(*ii*)	1:2	100	31.3	68.7
8	(*iii*)	1:2	94.1	26.9	67.2
9	(*iv*)	1:2	100	6.3	90.0
10	(*v*)	1:2	100	–	98.3

[a]) Reaction time: 50 min; all experiments were carried out at room temperature. (*i*) NBS/CH_2Cl_2, (*ii*) NBS/CH_2Cl_2/SiO_2, (*iii*) NBS/AcOH, (*iv*) KBr/$KBrO_3$/MeOH/H_2SO_4 (cat.), and (*v*) KBr/$KBrO_3$/AcOH. [b]) BA = brominating agent. [c]) Quantitative GC (*Ultra 2*) analysis.

ished when a substituent group is attached at the N-atom. This behavior is due to the presence of a bulky substituent such as Me, Ph, or $PhCH_2$ at the N-atom of the carbazole moiety and, at the same time, to the high molecular volume of the electrophile (Br^+).

We also studied the bromination of 2-methoxy-9-methyl-9*H*-carbazole (**4**). Thus, monobromination of **4** with 1 equiv. of NBS under neutral or acidic conditions gave the 3-bromocarbazole **4a**, which was the main product in *ca.* 80–90% yield, besides the 3,6-dibromocarbazole **4b** (*Table 4*, *Entries 1–3*). With 2 equiv. of NBS under neutral conditions, the 3,6-dibromocarbazole **4b** was obtained in 95% yield (*Entry 6*), whereas under acidic conditions, a significant amount of 1,3,6-tribromocarbazole **4c** was also

Table 4. *Bromination of 2-Methoxy-9-methyl-9*H*-carbazole* (**4**) *by Different Methods*

Entry	Method[a])	Carbazole **4**/BA[b]) [molar ratio]	Conversion [%]	Products [% yield][c])		
				4a	**4b**	**4c**
1	(*i*)	1:1	100	88.0	12.0	–
2	(*ii*)	1:1	100	81.8	10.9	–
3	(*iii*)	1:1	100	79.6	20.4	–
4	(*iv*)	1:1	100	–	74.1	23.9
5	(*v*)	1:1	100	–	89.3	8.3
6	(*i*)	1:2	100	5.0	95.0	–
7	(*ii*)	1:2	100	–	89.3	8.3
8	(*iii*)	1:2	100	–	63.7	34.2
9	(*iv*)	1:2	100	–	51.9	39.5
10	(*v*)	1:2	100	–	58.6	35.4
11	(*i*)	1:1[d])	90	89.5	–	–
12	(*i*)	1:2[d])	100	54.3	45.4	–

[a]) Reaction time: 15 min; all experiments were carried out at room temperature, unless indicated otherwise. (*i*) NBS/CH_2Cl_2, (*ii*) NBS/CH_2Cl_2/SiO_2, (*iii*) NBS/AcOH, (*iv*) KBr/$KBrO_3$/MeOH/H_2SO_4 (cat.), and (*v*) KBr/$KBrO_3$/AcOH. [b]) BA = brominating agent. [c]) Quantitative GC (*Ultra 2*) analysis. [d]) Method (*i*) at 0°.

formed (*Entries 7* and *8*). In all these reactions, a total consumption of the starting material was achieved. With 1 equiv. of the classical brominating agent, **4b** and **4c** were formed in *ca.* 3:1 and *ca.* 11:1 molar ratios for methods (*iv*) and (*v*), respectively (*Entries 4* and *5*). However, the corresponding **4b**/**4c** molar ratios with 2 equiv. are 4:3 and *ca.* 8:5, respectively (*Entries 9* and *10*).

These results encouraged us to perform the bromination at temperatures lower than room temperature (25°) to enhance the regioselectivity of the mono- and dibromination of compound **4**. Therefore, monobromination of **4** with 1 equiv. of NBS at 0° gave the 3-bromocarbazole **4a** in 90% yield as the only brominated product (*Table 4*, *Entry 11*), whereas with 2 equiv. of NBS, no improvement in the yield of **4b** was observed, **4a**/**4b** being obtained in a molar ratio close to 1:1 (*Entry 12*). Similar experiments were carried out at 0° with **4** and 1 or 2 equiv. of the traditional brominating agent, but no improvement was observed (results not shown).

The 2-(acetyloxy)-9*H*-carbazole (**5**), treated with 1 equiv. of NBS in CH_2Cl_2 under neutral or acidic conditions at room temperature, provided **5a** in *ca.* 50–65% yield, besides significant amounts of 6-bromocarbazole **5b** and 3,6-dibromocarbazole **5c** (*Table 5*, *Entries 1–3*). Monobromination of **5** could not be improved even if the reactions were carried out at 0°, which yielded a similar product distribution as at room temperature. With 2 equiv. of NBS in AcOH **5** provided 3,6-dibromocarbazole **5c** in a simple and clean reaction (*Entry 7*). However, the bromination of **5** with 2 equiv. of NBS in CH_2Cl_2 under neutral and acidic (SiO_2) conditions was not regioselective furnishing a mixture of 3-bromocarbazole **5a** and 3,6-dibromocarbazole **5c**, the latter being the main product (*Entries 5* and *6*). Bromination of **5** with KBr/$KBrO_3$ in MeOH doped with conc. sulfuric acid was not possible due to a rapid hydrolysis of the acetyloxy group of **5**. But 3,6-dibromocarbazole **5c** was obtained in 100% yield with 2 equiv. of

Table 5. *Bromination of 2-(Acetyloxy)-9*H*-carbazole* (**5**) *by Different Methods*

Entry	Method[a])	Carbazole **5**/BA[b]) [molar ratio]	Conversion [%]	Products [% yield][c])		
				5a	**5b**	**5c**
1	(*i*)	1:1	97.2	53.8	30.3	13.1
2	(*ii*)	1:1	93.1	65.5	17.6	8.4
3	(*iii*)	1:1	99.0	47.7	29.0	21.5
4	(*v*)	1:1	100	12.1	–	78.3
5	(*i*)	1:2	100	15.2	1.1	78.9
6	(*ii*)	1:2	100	38.5	–	61.5
7	(*iii*)	1:2	100	–	–	100
8	(*v*)	1:2	100	–	–	100

[a]) Reaction time: 15 min; all experiments were carried out at room temperature. (*i*) NBS/CH_2Cl_2, (*ii*) NBS/CH_2Cl_2/SiO_2, (*iii*) NBS/AcOH, and (*v*) KBr/$KBrO_3$/AcOH. [b]) BA = brominating agent. [c]) Quantitative GC (*Ultra 2*) analysis.

KBr/KBO_3 in AcOH (*Entry 8*), while when 1 equiv. of the brominating agent was used, a mixture of **5a** and **5c** was formed (*Entry 4*).

The bromination of 3-nitro-9*H*-carbazole (**6**) with NBS was carried out in CH_2Cl_2/THF 3:1 owing to the low solubility of **6** in CH_2Cl_2. When **6** was treated with 1 equiv. of NBS at room temperature under neutral and acidic conditions, 6-bromocarbazole **6a** was formed in 70% yield as the only product (*Table 6*, *Entries 1–3*). With 2 equiv. of NBS, **6a** was obtained selectively in 89–100% yield both under neutral and acidic conditions (*Entries 6–8*). Similar results were obtained with 1 or 2 equiv. of KBr/$KBrO_3$ (*Entries 4, 5, 9,* and *10*).

Table 6. *Bromination of 3-Nitro-9*H*-carbazole* (**6**) *by Different Methods*

Entry	Method[a])	Carbazole **6**/BA[b]) [molar ratio]	Conversion [%]	**6a** [% yield][c])
1	(*i*)	1:1	74.4	71.2
2	(*ii*)	1:1	73.9	70.6
3	(*iii*)	1:1	67.9	62.7
4	(*iv*)	1:1	100	80.2
5	(*v*)	1:1	33.2	31.1
6	(*i*)	1:2	99	95.9
7	(*ii*)	1:2	100	100
8	(*iii*)	1:2	100	89.3
9	(*iv*)	1:2	100	100
10	(*v*)	1:2	73.4	70.8

[a]) Reaction time: 45 min; all experiments were carried out at room temperature. (*i*) NBS/CH_2Cl_2/THF, (*ii*) NBS/CH_2Cl_2THF/SiO_2, (*iii*) NBS/AcOH, (*iv*) KBr/$KBrO_3$/MeOH/H_2SO_4 (cat.), and (*v*) KBr/$KBrO_3$/AcOH. [b]) BA = brominating agent. [c]) Quantitative GC (*Ultra 2*) analysis.

Semiempirical Calculations. As known, the high reactivity of the aromatic ring of carbazole in electrophilic substitution makes it highly probable that these reactions reflect the established Br^+ activity of the different brominating systems. Also, the experimental results obtained in the bromination of carbazoles show a preferential sub-

stitution pattern which is the C(3) and/or C(6) *para*-substitution with respect to the N-atom. This was confirmed by the net atomic-charge values calculated by using the semi-empirical PM3 method, as implemented in the version of the HyperChem 7.0 Suite program [25] to obtain the optimized geometry of carbazoles **1**–**6** and bromocarbazole derivatives. As can be seen from the static charge-distribution pattern in carbazoles **1**–**6** and their bromocarbazole derivatives (*Table 7*), the calculated preferential electrophilic substitution positions (kinetic attack) are in agreement with the experimental results obtained.

Table 7. *Calculated Static Charge Distribution*[a])

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
1	−0.108	−0.082	−0.126	−0.050				
1b	−0.103	−0.065	−0.131	−0.030	−0.047	−0.125	−0.079	−0.108
1d	−0.116	−0.056	−0.141	−0.017	−0.018	−0.140	−0.056	−0.113
2	−0.109	−0.083	−0.124	−0.050	−0.049	−0.125	−0.079	−0.116
2a	−0.104	−0.066	−0.131	−0.029	−0.045	−0.124	−0.076	−0.116
2b	−0.104	−0.063	−0.132	−0.026	−0.024	−0.133	−0.059	−0.110
3	−0.115	−0.081	−0.129	−0.048				
3a	−0.116	−0.078	−0.128	−0.044	−0.028	−0.133	−0.064	−0.108
3b	−0.108	−0.061	−0.134	−0.024				
4	−0.195	0.111	−0.165	−0.016	−0.056	−0.122	−0.087	−0.105
4a	−0.190	0.128	−0.186	0.008	−0.053	−0.121	−0.085	−0.104
4b	−0.191	0.132	−0.187	0.012	−0.033	−0.128	−0.068	−0.099
4c	−0.198	0.166	−0.197	0.021	−0.030	−0.130	−0.065	−0.100
5	−0.120	0.060	−0.153	−0.032	−0.047	−0.124	−0.078	−0.105
5a	−0.171	0.104	−0.174	0.000	−0.047	−0.121	−0.079	−0.104
5b	−0.120	0.065	−0.152	−0.028	−0.027	−0.132	−0.061	−0.100
5c	−0.172	0.109	−0.175	0.004	−0.027	−0.131	−0.061	−0.098
6	−0.137	0.010	−0.447	0.055	−0.065	−0.116	−0.076	−0.101
6a	−0.135	0.012	−0.444	0.059	−0.024	−0.131	−0.058	−0.095

[a]) Calculations were performed by using the PM3 method [25].

It is interesting to mention that, even though the highest negative-charge densities are localized at C(1) and C(3) and also at C(6) and C(8), the experimental results show an almost exclusive tendency for *para*-bromination with respect to the substituted N-atom of the carbazoles (see the product distribution obtained from **1** (R^1 = Me), **2** (R^1 = Ph), **3** (R^1 = $PhCH_2$), and **4** (R^1 = Me)). These results can be explained by the large volume of the Br^+ ion hindering its approach to the *ortho*-position, particularly in case of compounds **2**–**4**. A similar steric effect is observed for 2-(acetyloxy)-9*H*-carbazole (**5**) where the AcO group, which is bulky enough, hinders the Br^+ approach to the *ortho*-position C(1), and where the incoming electrophile attacks exclusively the unhindered *para*-positions C(3) and C(6). In conclusion, it seems certain that electrophilic attack of carbazole under a variety of conditions occurs preferentially at the C-atoms with charge densities higher than −0.095 when no steric hindrance is present.

Spectroscopy of Carbazoles and Bromocarbazole Derivatives. The absorption spectra of carbazoles and bromocarbazole derivatives in MeCN at 298 K generally exhibit three bands in the 255–280, 275–305, and 305–370 nm region, as shown in the *Figure*

for 9-methyl-9*H*-carbazole (**1**) and its bromo derivatives **1b** and **1d**. Previous spectroscopic studies and theoretical calculations have been carried out [26] allowing for unambiguous assignment of the lowest-lying excited electronic states of carbazoles as ^1L_a and ^1L_b in the C_{2v} symmetry point group with the short (z) axis and long (y) axis respectively in the plane of the molecule. Comparing the position and oscillator strength of the bands located in the 300- and 350-nm region of the bromocarbazoles with that of carbazoles, it is possible to assign them to ^1L_a ($S_2 - S_0$) and ^1L_b ($S_1 - S_0$) electronic transitions too (see *Fig.*).

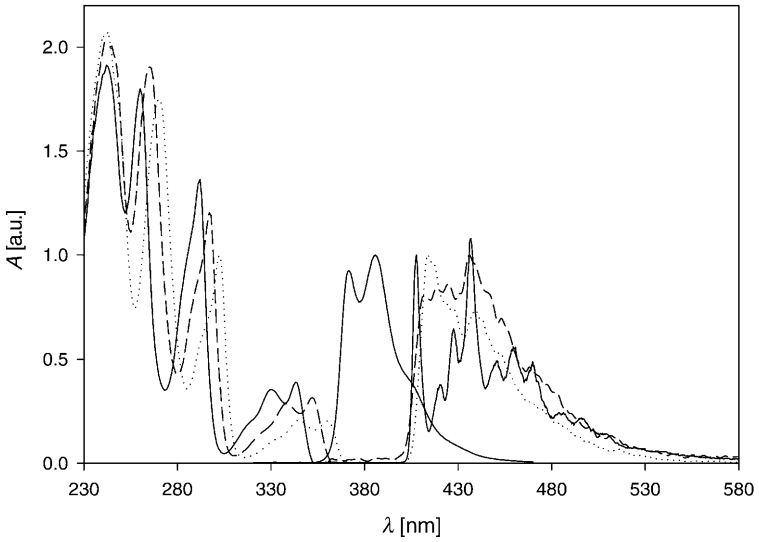


Figure. *Electronic absorption and fluorescence emission spectra* (MeCN; 298 K) *and phosphorescence emission spectra* (solid matrix; 77 K) *of 9-methyl-9*H*-carbazole* (**1**; ——), *3-bromo-9-methyl-9*H*-carbazole* (**1b**; – – –), *and 3,6-dibromo-9-methyl-9*H*-carbazole* (**1d**; ·····). Concentration: $1.0 \cdot 10^{-5}$ M; λ_{exc} 320 nm.

The absorption spectra of the bromocarbazole derivatives exhibit a noticeable bathochromic shift of the ^1L_b band ranging from 10 to 19 nm compared to that of the carbazoles **1**–**6** (see *Table 8*). In general, the absorption spectra of bromocarbazoles show a small bathochromic shift of the other two electronic transition bands with respect to carbazoles **1**–**6**. In the *Figure*, these smaller bathochromic shifts can be seen for 9-methyl-9*H*-carbazole (**1**) and its bromo derivatives **1b** and **1d**, which range from 6 to 10 nm, as the number of Br-atoms attached to the carbazole moiety increases. This significant red shift observed when the Br-atom is located at C(3) and/or C(6) of the carbazole moiety can be interpreted in terms of mesomeric and/or inductive effects due to the higher electronic density of the Br-atom as compared to the H-atom at C(3) and/or C(6) [27].

The carbazoles **1**–**5** are good fluorescent chromophores with ϕ_f values ranging from 0.35 to 0.45 and τ_f values in the order of 11.4–14.7 ns (see *Table 8*). These compounds display mirror symmetry when the fluorescent emission and absorption spectra are compared, as shown for the spectra of 9-methyl-9*H*-carbazole (**1**) in the *Figure*. This

indicates that the geometries of the molecules are quite similar in their ground and excited states. For 3-nitro-9*H*-carbazole (**6**), no fluorescence emission was detected due to a high spin–orbital coupling between the nitro group and the carbazole moiety [27][28]. A similar behavior is expected for the bromocarbazole derivatives **1b**,**d**, **2a**,**b**, **3a**,**b**, **4b**,**c**, and **5a**,**c** where a higher spin–orbital-coupling mechanism operates as the number of Br-atoms attached to the carbazole moiety is increased. Thus, no fluorescence emission was detected for these compounds in MeCN solutions at 298 K, and it can be concluded that these molecules dissipate efficiently the energy from the electronic singlet excited state (S_1) through radiationless processes such as internal conversion and/or intersystem crossing processes.

We also measured the phosphorescence emission spectra of carbazoles **1**–**6** and their bromo derivatives in a solid matrix at 77 K, and compounds **1b**,**d**, **2a**,**b**, **3a**,**b**, **4b**,**c**, and **5a**,**c** showed to be good phosphorescent chromophores. The maxima wavelength values of phosphorescence emission, λ_{max}(phosph), are collected in *Table 8* and, in general, these values are located between 408 and 428 nm. The *Figure* shows the phosphorescence emission spectra of compounds **1**, **1b**, and **1d**. The λ_{max}(phosph) values of the bromocarbazole derivatives exhibit a bathochromic shift ranging between 9 and 17 nm compared to that of the carbazoles **1**–**5**. This behavior accounts for the increase of the charge density in the carbazole moiety due to the presence of the Br-substituent at C(3) and/or C(6) and can be interpreted by inductive and/or mesomeric effects [27]. In this connection, it is worthy to mention that the shapes of the phosphorescence emission spectra of bromocarbazole derivatives **1b**,**d**, **2a**,**b**, **3a**,**b**, **4b**,**c**, and **5a**,**c** are similar to that of the carbazoles **1**–**5** (see *Fig.* for **1**, **1b**, and **1d**). Taking into account

Table 8. *Spectroscopic Data* (λ_{max}), *Fluorescence Quantum Yield* (ϕ_f) *and Phosphorescence Quantum Yield* (ϕ_p) *of Carbazoles and Bromocarbazoles in MeCN at 298 K and in a Solid Matrix at 77 K*

	λ_{max}(abs) [nm][a])	λ_{max}(fluo) [nm][a])	λ_{max}(phosph) [nm][b])	ϕ_f[a])	τ_f [ns][c])	ϕ_p[b])
1	345	356	408	0.43	14.7	0.24
1b	355	[d])	414	[d])	–	0.56
1d	362	[d])	417	[d])	–	0.74
2	342	358	407	0.34	11.4	0.35
2a	352	[d])	415	[d])	–	0.69
2b	361	[d])	424	[d])	–	0.88
3	342	355	410	0.40	12.3	0.47
3a	351	[d])	415	[d])	–	0.70
3b	357	[d])	425	[d])	–	0.99
4	330	350	412	0.45	14.3	0.23
4b	342	[d])	426	[d])	–	0.77
4c	349	[d])	428	[d])	–	0.94
5	332	340	409	0.45	13.2	0.24
5a	343	[d])	420	[d])	–	0.71
5c	349	[d])	424	[d])	–	0.96
6	365	[d])	480	[d])	–	0.04
6a	365	[d])	481	[d])	–	> 0.001

[a]) Measured in MeCN at 298 K. [b]) Measured in the solid matrix ^{i}PrOH/Et_2O 1:1 at 77 K. [c]) Values taken from [26a]. [d]) No fluorescence detected.

that the shape of the phosphorescence emission spectra of these compounds are 'naphthalene-like' and considering that the phosphorescence lifetime (τ_p) is in the time scale of seconds, we concluded that the electronic excited triplet state is most likely due to a π,π^* electronic transition [28]. A similar conclusion was previously reported for 9*H*-carbazole, 3-bromo-9*H*-carbazole, and 3,6-dibromo-9*H*-carbazole [26a]. It is noteworthy to mention that the bromocarbazole derivatives show no fluorescence emission in a solid matrix at 77 K, while carbazoles **1**–**6** are good fluorescent and phosphorescent chromophores under the same experimental conditions [26a]. These results confirm that the spin–orbital-coupling mechanism operates to a great extent in bromocarbazoles in a solid matrix at 77 K, and the deactivation of the singlet excted state (S_1) through radiationless processes takes place efficiently. Also, under these experimental conditions, population of the triplet excited state (T_1) of bromocarbazoles **1b**,**d**, **2a**,**b**, **3a**,**b**, **4b**,**c**, and **5a**,**c** seems to be very efficient because these compounds show ϕ_p values ranging between 0.56 to 0.99 (*Table 8*).

In the case of 6-bromo-3-nitro-9*H*-carbazole (**6a**), no red shift of λ_{max}(phosph) was observed in comparison with 3-nitrocarbazole (**6**). The ϕ_p values of **6** and **6a** are lower than 0.05, and we conclude that the deactivation of the triplet excited state (T_1) takes place efficiently through a radiationless process (internal conversion) where the radiative process (phosphorescence emission) does not compete to a greater extent. Taking into account that the phosphorescene emission spectra of compounds **6** and **6a** are quite similar and are 'benzophenone-like', we conclude that the electronic triplet excited state is most likely to be due to an n,π^* electronic transition [28].

In conclusion, the spectroscopic study shows that bromocarbazoles **1b**,**d**, **2a**,**b**, **3a**,**b**, **4b**,**c**, **5a**,**c**, and **6a** are not fluorescent chromophores and populate efficiently the lowest triplet excited state. In this regard, these compounds could be considered as possible samples for studying the photoinduced heterolytic cleavage of the C–Br bond taking into account that the photoreaction takes place efficiently from the lowest triplet excited state.

Conclusions. – The regioselectivity of the bromination reaction of *N*- and *C*-substituted carbazoles **1**–**6** was improved when 1 equiv. of NBS/CH_2Cl_2 at room temperature was used as brominating agent. Thus, monobromocarbazole derivatives were obtained as the main product with chemical yields higher than 75%. Acidic conditions (NBS/SiO_2 and NBS/AcOH) diminished significantly the regioselectivity of the monobromination. Dibromocarbazole derivatives were obtained with high regioselectivity when 2 equiv. of NBS/CH_2Cl_2 were used as brominating agent, as well as when 2 equiv. of KBr/$KBrO_3$ under acidic condition were employed. Theoretical calculations of the static charge distributions in carbazoles **1**–**6** correlated with the experimental results, and the preferential sites of kinetic attack by the incoming electrophile Br^+ were nicely predicted.

The carbazoles **1**–**5** and their bromo derivatives **1b**,**d**, **2a**,**b**, **3a**,**b**, **4b**,**c**, and **5a**,**c**, showed a noticeable bathochromic shift in the absorption and phosphorescence emission spectra at 298 and 77 K as the number of Br-atoms attached to the carbazole moiety increased. This red shift is due to mesomeric and/or inductive effects arising from the higher electronic density of the Br-atom as compared to a H-atom at C(3) and/or C(6). Also, these bromocarbazole derivates are good phosphorescent chromophores

in solid matrix at 77 K due to a high spin–orbital-coupling mechanism between the Br-atoms and the carbazole moiety with ϕ_p values in the range 0.23–0.99. The shape of the phosphorescence emission spectra of these compounds are 'naphthalene-like', and taking into account the phosphorescence lifetime values, the lowest triplet excited state is most likely due to a π,π^* electronic transition. In the case of compounds **6** and **6a**, the 'benzophenone-like' shape of the phosphorescent emission spectra indicates that the lowest triplet excited state is due to an n,π^* electronic transition. The effect of a Br-atom on the n,π^* transitions is very minor because compounds **6** and **6a** showed similar absorption and phosphorescence spectra (*Table 8*).

In conclusion, the regioselectivity of the brominaton reaction provides an alternative method for the synthesis of selected bromo-substituted heterocyclic compounds which are not commercially available. These compounds are interesting species to be tested as substrates for the study of the photoinduced heterolytic cleavage reaction of the C–Br bond. In this regard, spectroscopic and photophysical analyses of bromocarbazole derivatives are required to assess which lowest excited state (singlet or triplet state) is efficiently populated. Thus, we could determine that compounds **1b**,**d**, **2a**,**b**, **3a**,**b**, **4b**,**c**, **5a**,**c**, and **6a** populate their lowest triplet excited states efficiently and, from these results, we expect that the photoinduced heterolytic cleavage reaction will take place as well. Further studies regarding this photochemical reaction is in progress in our laboratory.

The authors thank the Universidad de Buenos Aires (X022), CONICET (PIP05/5443), and ANPCyT (PICT 6-12312) for partial financial support. We are grateful to Dr. *H. Nonami* (Ehime University, Japan) for providing the HyperChem Suite 7.0. *R. E.-B.*, *F. M. C.,* and *S. M. B.* are research members of CONICET.

Experimental Part

General. CH_2Cl_2, $CHCl_3$, MeOH, AcOH, hexane, AcOEt, and other reagents used were of anal. grade. Solvents were freshly distilled and dried before use. MeCN, ^{i}PrOH, and Et_2O were of UV spectrograde and were purchased from *J. T. Baker*. The 9-methyl-9*H*-carbazole (**1**), 9-phenyl-9*H*-carbazole (**2**), 9*H*-carbazole, and *N*-bromosuccinimide (NBS) were purchased from *Aldrich*. The 9*H*-carbazol-2-ole was purchased from *Aldrich* and recrystallized from EtOH before used. The 2-methoxy-9-methyl-9*H*-carbazole (**4**) [29], 9-benzyl-9*H*-carbazole (**3**) [30], 2-(acetyloxy)-9*H*-carbazole (**5**) [31], and 3-nitro-9*H*-carbazole (**6**) [32] were prepared according to the procedures described in the literature. TLC: *Merck* aluminium silica gel sheets (0.2 mm layer thickness, silica gel *60* F_{254}). Column chromatography (CC): *Merck* silica gel *60* (0.040–0.063 mm); FC = flash chromatography. Gas chromatography (GC): *Hewlett Packard 5890* with an *Ultra-2-Hewlett-Packard* capillary column (crosslinked 5% phenylpolysiloxane; 30 m × 0.25 mm × 0.50 μm); gas carrier N_2; FID detector. Melting points: *Fisher-Jones* apparatus; not corrected. UV/VIS Spectra: *UV-1203-UV-VIS Shimadzu* spectrophotometer. Fluorescence and phosphorescence spectra: *Perkin-Elmer-LS-50* spectrofluorometer; fluorescence quantum yield determination in MeCN at 298 K in the same apparatus relative to that of quinine sulfate in 0.1M $HClO_4$ [26]; phosphorescence quantum yield determination in a solid matrix of ^{i}PrOH/Et_2O 1:1 at 77 K in the same apparatus relative to that of carbazole [26]. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-AC-200* and *Bruker-500* spectrometer; chemical shifts δ in ppm rel. to internal $SiMe_4$, *J* in Hz; standard pulse sequences. EI-MS: *VG-ZAB-BEQ* instrument; in *m*/*z* (rel %).

Theoretical Calculations. The ground-state geometry and static charge distribution of carbazoles **1**–**6** and bromocarbazole derivatives were calculated by using the semi-empirical parameterized PM3 method

as implemented in version 7.0 of the HyperChem Program [25] which is established to be effective in studies of molecules containing heteroatoms, compared with other methods such as MINDO/3 or MNDO.

Bromination Reaction of Carbazoles **1**–**6** *with NBS and NBS/Silica Gel in CH_2Cl_2. General Procedure 1* (*G.P. 1*).To a stirred soln. of each carbazole **1**–**6** (0.55 mmol) in CH_2Cl_2 (10 ml) containing silica gel (6 g) (or not depending on the brominating method used), a soln. of NBS (0.55 to 1.10 mmol depending on the stoichiometry used) in CH_2Cl_2 (5 ml) was added dropwise. The mixture was stirred for an appropriate time in the absence of light at r.t. under normal (air) atmosphere (TLC silica gel *60* F_{245}, hexane/AcOEt mixtures) and GC (*Ultra-2-HP*) monitoring. The mixture was then filtered and the silica gel washed with CH_2Cl_2 (3×15 ml). The combined filtrate was washed with H_2O (2×50 ml), dried (Na_2SO_4), and evaporated. The brownish solid residue was dissolved in the minimum volume of CH_2Cl_2, this soln. mixed with silica gel *60* and evaporated, and the brownish residue put on top of a prep. column and subjected to FC (silica gel, hexane/AcOEt mixtures). The isolated products were characterized by m.p., ^{1}H- and ^{13}C-NMR, MS and microanalysis.

The same procedure was applied to the brominations with NBS/AcOH replacing the solvent CH_2Cl_2 by AcOH.

Bromination Reaction of Carbazoles **1**–**6** *With $KBrO_3$/KBr/Catalytic Acid Systems. General Procedure 2 (G.P. 2)*. To a stirred soln. of each carbazole **1**–**6** (0.55 mmol) in MeOH (20 ml), solid KBr (0.15 to 0.30 mmol depending on the stoichiometry used) and $KBrO_3$ (0.28 to 0.56 mmol depending on the stoichiometry used) were added. Then, conc. sulfuric acid (42 µl to 0.84 ml depending on the stoichiometry used; d = 1.85 g/ml) was added dropwise. The mixture was stirred for an appropriate time in the absence of light at r.t. under normal (air) atmosphere (TLC silica gel *60* F_{245}, hexane/AcOEt mixtures) and GC (*Ultra-2-HP*) monitoring). The mixture was then neutralized with 10% aq. Na_2CO_3 soln. and extracted with CH_2Cl_2 (3×15 ml), the org. phase washed with H_2O (3×20 ml), dried (Na_2SO_4) and evaporated, the brownish solid residue dissolved in the minimum volume of CH_2Cl_2, this soln. mixed with silica gel *60* and evaporated, and the brownish solid residue put on top of a prep. column and subjected to FC (silica gel, hexane/AcOEt mixtures). The isolated products were characterized by m.p., ^{1}H- and ^{13}C-NMR, MS and microanalysis.

The same procedure was applied to the brominations with KBr/$KBrO_3$/AcOH replacing the solvent MeOH by AcOH.

*1-Bromo-9-methyl-9*H-*carbazole* (**1a**). White needles (hexane). M.p. 60°. ^{1}H-NMR ($CDCl_3$, 500 MHz): 8.25 (*dd*, *J* = 2.0, 8.2, H–C(4)); 8.09 (*d*, *J* = 8.0, H–C(5)); 7.54 (*dd*, *J* = 2.0, 7.9, H–C(2)); 7.50 (*t*, *J* = 8.0, H–C(6)); 7.39–7.23 (*m*, H–C(7), H–C(8)); 7.17 (*t*, *J* = 8.2, H–C(3)); 3.82 (*s*, Me–N(9)). EI-MS (70 eV): 261 (98.7), 259 (100, M^+), 246 (5.6), 244 (5.0, $[M-Me]^+$), 181 (16.3), 179 (20.2, $[M-Br]^+$), 165 (10), 164 (9.4), 139 (6.0). Anal. calc. for $C_{13}H_{10}BrN$ (260.13): C 60.02, H 3.87, Br 30.72, N 5.38; found: C 59.93, H 3.85, Br 30.81, N 5.41.

*3-Bromo-9-methyl-9*H-*carbazole* (**1b**). White needles (hexane). M.p. 78–79°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.18 (*d*, *J* = 2.1, H–C(4)); 8.01 (*d*, *J* = 8.1, H–C(5)); 7.54 (*dd*, *J* = 2.1, 7.9, H–C(2)); 7.50 (*t*, *J* = 8.11, H–C(6)); 7.38–7.24 (*m*, H–C(7), H–C(8)); 7.17 (*d*, *J* = 7.9, H–C(1)); 3.83 (*s*, Me–N(9)). ^{13}C-NMR ($CDCl_3$, 200 MHz): 141.2 (C(9a)); 139.5 (C(8a)); 128.2 (C(4)); 126.4 (C(5)); 124.4 (C(4a)); 123.0 (C(6)); 121.7 (C(4b)); 120.5 (C(2)); 119.3 (C(7)); 111.6 (C(3)); 109.9 (C(1)); 108.7 (C(8)); 29.1 (Me–N(9)). EI-MS (70 eV): 261 (98.9), 259 (100, M^+), 246 (4.8), 244 (4.0, $[M-Me]^+$), 181 (12.6), 179 (19.2, $[M-Br]^+$), 165 (9), 164 (8.3), 139 (4.0). Anal. calc. for $C_{13}H_{10}BrN$ (260.13): C 60.02, H 3.87, Br 30.72, N 5.38; found: C 59.95, H 3.85, Br 30.84, N 5.40.

*1,6-Dibromo-9-methyl-9*H-*carbazole* (**1c**). White needles (hexane). M.p. 123°. ^{1}H-NMR ($CDCl_3$, 500 MHz): 8.25 (*dd*, *J* = 2.0, 8.2, H–C(4)); 8.13 (*d*, *J* = 2.3, H–C(5)); 7.60 (*dd*, *J* = 2.3, 8.5, H–C(7)); 7.44 (*dd*, *J* = 2.0, 8.0, H–C(2)); 7.28 (*d*, *J* = 8.5, H–C(8)); 7.18 (*t*, *J* = 8.0, H–C(3)); 3.82 (*s*, Me–N(9)). EI-MS (70 eV): 341 (39), 339 (91, M^+), 337 (42.2), 324 (6), 323 (10, $[M-Me]^+$), 321 (5.2), 261 (35.2), 259 (43.1, $[M-Br]^+$), 179 (21), 168 (18.3), 167 (37), 164 (17.1), 138 (5). Anal. calc. for $C_{13}H_9Br_2N$ (339.03): C 46.06, H 2.68, Br 47.14, N 4.13; found: C 45.95, H 2.67, Br 47.31, N 4.15.

*3,6-Dibromo-9-methyl-9*H-*carbazole* (**1d**). White plates (hexane). M.p. 141°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.13 (*d*, *J* = 2.0, H–C(4), H–C(5)); 7.57 (*dd*, *J* = 2.0, 8.5, H–C(2), H–C(7)); 7.27 (*d*, *J* = 8.5, H–C(1), H–C(8)); 3.85 (*s*, Me–N(9)). ^{13}C-NMR ($CDCl_3$, 200 MHz): 139.8 (C(8a), C(9a)); 129.0 (C(4),

C(5)); 123.3 (C(4a), C(4b)); 123.2 (C(2), C(7)); 112.0 (C(3), C(6)); 110.1 (C(8), C(1)); 29.2 (Me–N(9)). EI-MS (70 eV): 341 (38.8), 339 (90.3, M^+), 337 (43.8), 324 (5), 323 (10, $[M-Me]^+$), 321 (4.8), 261 (36.4), 259 (42.1, $[M-Br]^+$), 179 (20.5), 168 (18.2), 167 (39.5), 164 (16.7), 138 (5). Anal. calc. for $C_{13}H_9Br_2N$ (339.03): C 46.06, H 2.68, Br 47.14, N 4.13; found: C 45.93, H 2.67, Br 47.30, N 4.16.

*3-Bromo-9-phenyl-9*H-*carbazole* (**2a**). White needles (hexane). M.p. 98°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.22 (*d*, *J* = 2.1, H–C(4)); 8.12 (*d*, *J* = 8.2, H–C(5)); 7.67–7.54 (*m*, H–C(2), H–C(7)); 7.53 (*m*, 2 H_o); 7.40 (*m*, 2 H_m, H_p); 7.28 (*dd*, *J* = 8, H–C(6)); 7.30 (*d*, *J* = 7.9, H–C(1)); 7.29 (*d*, *J* = 8.1, H–C(8)). ^{13}C-NMR ($CDCl_3$, 200 MHz): 141.3 (C(9a)); 139.6 (C(8a)); 137.3 (C_{ispo}); 130.1 (C_o); 128.6 (C_m); 127.8 (C(4)); 127.1 (C_p); 126.7 (C(5)); 125.2 (C(4a)); 123.1 (C(6)); 122.4 (C(4a)); 120.5 (C(2)); 120.4 (C(7)); 112.8 (C(3)); 111.3 (C(1)); 110.0 (C(8)). EI-MS (70 eV): 323 (100), 321 (90, M^+), 243 (23.5, $[M-Br]^+$), 241 (53.7), 166 (30.4, $[M-Br-Ph]^+$), 139 (3.4), 138 (5), 137 (4). Anal. calc. for $C_{18}H_{12}BrN$ (322.20): C 67.10, H 3.75, Br 24.80, N 4.35; found: C 66.23, H 3.77, Br 24.75, N 4.33.

*3,6-Dibromo-9-phenyl-9*H-*carbazole* (**2b**). White plates (hexane). M.p. 159–160°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.20 (*d*, *J* = 8.2, H–C(4), H–C(5)); 7.60 (*t*, *J* = 8.0, 2 H_o); 7.55–7.45 (*m*, H–C(2), H–C(7), 2 H_m, H_p); 7.24 (*d*, *J* = 8.0, H–C(1), H–C(8)). ^{13}C-NMR ($CDCl_3$, 200 MHz): 139.8 (C(8a), C(9a)); 136.8 (C_{ipso}); 130.1 (C_o); 129.4 (C_m); 128.1 (C(4), C(5)); 126.9 (C_p); 123.8 (C(4a), C(4b)); 123.2 (C(2), C(7)); 113.1 (C(3), C(6)); 111.5 (C(1), C(8)). EI-MS (70 eV): 403 (43), 401 (76.5, M^+), 399 (41.2), 323 (6.5), 321 (7.2, $[M-Br]^+$), 241 (40), 239 (22), 168 (4), 167 (38), 164 (9), 139 (2), 137 (5). Anal. calc. for $C_{18}H_{11}Br_2N$ (401.10): C 53.90, H 2.76, Br 39.84, N 3.49; found: C 53.86, H 2.75, Br 39.91, N 3.48.

*3-Bromo-9-benzyl-9*H-*carbazole* (**3a**). White needles (hexane). M.p. 111–112°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.25 (*d*, *J* = 2.1, H–C(4)); 8.09 (*dd*, *J* = 2.4, 8.1, H–C(5)); 7.51 (*dd*, *J* = 2.1, 7.9, H–C(2)); 7.44 (*dd*, *J* = 1.9, 7.5, H–C(7)); 7.40 (*m*, 2 H_o); 7.31–7.21 (*m*, H–C(6), 2 H_m, H_p); 7.22 (*d*, *J* = 7.5, H–C(8)); 7.12 (*d*, *J* = 7.9, H–C(1)); 5.5 (*s*, PhCH_2). ^{13}C-NMR ($CDCl_3$, 200 MHz): 141.0 (C(9a)); 139.3 (C(8a)); 136.7 (C_{ipso}); 128.9 (C_o); 128.5 (C_m); 127.6 (C(4)); 126.6 (C(5)); 126.3 (C_p); 124.8 (C(4b)); 123.2 (C(6)); 122.0 (C(4a)); 120.6 (C(2)); 119.6 (C(7)); 112.1 (C(3)); 110.4 (C(1)); 109.2 (C(8)); 46.7 (Ph*C*H$_2$). EI-MS (70 eV): 337 (17), 335 (17, M^+), 257 (22, $[M-Br]^+$), 246 (2, $[M-C_6H_5CH_2]^+$), 244 (2), 167 (8), 166 (4), 165 (5), 91 (100, $C_6H_5CH_2^+$). Anal. calc. for $C_{19}H_{14}BrN$ (336.23): C 67.87, H 4.20, Br 23.77, N 4.17; found: C 67.81, H 4.18, Br 23.82, N 4.18.

*3,6-Dibromo-9-benzyl-9*H-*carbazole* (**3b**). White plates (hexane). M.p. 156–157°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.16 (*d*, *J* = 2.1, H–C(4), H–C(5)); 7.52 (*dd*, *J* = 2.1, 8.3, H–C(2), H–C(7)); 7.30–7.25 (*m*, 2 H_m, H_p); 7.21 (*d*, *J* = 8.3, H–C(1), H–C(8)); 7.06 (*dd*, *J* = 1.9, 7.9, 2 H_o); 5.45 (*s*, PhCH_2). ^{13}C-NMR ($CDCl_3$, 200 MHz): 139.4 (C(9a), C(8a)); 136.2 (C_{ipso}); 129.3 (C_o); 128.9 (C_m); 127.8 (C(4), C(5)); 126.3 (C_p); 123.6 (C(4a), C(4b)); 123.3 (C(2), C(7)); 112.5 (C(3), C(6)); 110.7 (C(1), C(8)); 46.8 (Ph*C*H$_2$). EI-MS (70 eV): 417 (25), 415 (48, M^+), 413 (26), 335 (3, $[M-Br]^+$), 333 (2), 255 (3), 164 (13), 91 (100, $C_6H_5CH_2^+$). Anal. calc. for $C_{19}H_{13}Br_2N$ (415.12): C 54.97, H 3.16, Br 38.50, N 3.37; found: C 54.85, H 3.14, Br 38.63, N 3.39.

*3-Bromo-2-methoxy-9-methyl-9*H-*carbazole* (**4a**). White needles (hexane). M.p. 140°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.20 (*s*, H–C(4)); 7.96 (*dd*, *J* = 2.1, 8.2, H–C(5)); 7.47–7.33 (*m*, *J* = 2.2, 7.9, H–C(6), H–C(7)); 7.25 (*dd*, H–C(8)); 6.83 (*s*, H–C(1)); 4.02 (*s*, MeO); 3.80 (*s*, MeN). ^{13}C-NMR ($CDCl_3$, 200 MHz): 154.5 (C(2)); 141.1 (C(8a)); 141.0 (C(9a)); 125.0 (C(7)); 124.5 (C(4)); 121.9 (C(4b)); 119.4 (C(5)); 119.3 (C(6)); 117.3 (C(4a)); 108.4 (C(8)); 102.8 (C(3)); 92.0 (C(1)); 56.5 (MeO); 29.2 (MeN). EI-MS (70 eV): 291 (22), 289 (24, M^+), 276 (7), 274 (7, $[M-Me]^+$), 261 (23), 259 (23, $[M-MeO]^+$), 248 (9.3), 246 (12.5), 195 (8.4), 179 (8.7, $[M-MeO-Br]^+$), 167 (47.2), 166 (4.3), 164 (5.1). Anal. calc. for $C_{14}H_{12}BrNO$ (290.16): C 57.95, H 4.17, Br 27.54, N 4.83; found: C 57.82, H 4.15, Br 27.64, N 4.86.

*3,6-Dibromo-2-methoxy-9-methyl-9*H-*carbazole* (**4b**). White plates (hexane). M.p. 181°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.09 (*s*, H–C(4)); 7.99 (*d*, *J* = 2.3, H–C(5)); 7.47 (*dd*, *J* = 2.3, 8.1, H–C(7)); 7.17 (*d*, *J* = 8.1, H–C(8)); 6.76 (*s*, H–C(1)); 4.01 (*s*, MeO); 3.73 (*s*, MeN). ^{13}C-NMR ($CDCl_3$, 200 MHz): 155.1 (C(2)); 141.5 (C(8a)); 139.5 (C(9a)); 127.5 (C(7)); 124.7 (C(4)); 123.6 (C(4b)); 122.3 (C(5)); 116.1 (C(4a)); 112.2 (C(6)); 109.9 (C(8)); 103.4 (C(3)); 92.0 (C(1)); 56.5 (MeO); 29.3 (MeN). EI-MS (70 eV): 371 (54), 369 (100, M^+), 367 (53), 356 (12.5), 354 (24.1, $[M-Me]^+$), 352 (11.6), 327 (16.5), 325 (28.9, $[M-MeO]^+$), 324 (15.4), 247 (11.2), 245 (10.3), 166 (12), 165 (4). Anal. calc. for $C_{14}H_{11}Br_2NO$ (369.05): C 45.56, H 3.00, Br 43.30, N 3.80; found: C 45.43, H 2.98, Br 43.41, N 3.82.

*1,3,6-Tribromo-2-methoxy-9-methyl-9*H-*carbazole* (**4c**). White plates (hexane). M.p. 198°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.10 (*s*, H–C(4)); 7.99 (*d*, *J* = 2.0, H–C(5)); 7.45 (*dd*, *J* = 2.0, 8.0, H–C(7)); 7.15 (*d*, *J* = 8.0, H–C(8)); 4.01 (*s*, MeO), 3.72 (*s*, MeN). ^{13}C-NMR ($CDCl_3$, 200 MHz): 155.1 (C(2)); 141.5 (C(8a)); 139.5 (C(9a)); 127.6 (C(7)); 124.8 (C(4)); 123.6 (C(4b)); 122.3 (C(5)); 116.2 (C(4a)); 112.1 (C(6)); 109.9 (C(8)); 103.4 (C(3)); 104.3 (C(1)); 56.5 (MeO); 29.3 (MeN). EI-MS (70 eV): 453 (2.2), 451 (9.3), 449 (12.1, M^+), 447 (8.5), 445 (2.1), 371 (43), 369 (100, $[M-Br]^+$), 367 (45), 356 (12.5), 354 (24.1, $[M-Me]^+$), 352 (11.6), 327 (17), 325 (28.9, $[M-MeO]^+$), 324 (15.4), 247 (11.2), 245 (13), 166 (12), 165 (4). Anal. calc. for $C_{14}H_{10}Br_3NO$ (447.95): C 37.54, H 2.25, Br 53.51, N 3.13; found: C 37.62, H 2.27, Br 53.38, N 3.12.

*2-(Acetyloxy)-3-bromo-9*H-*carbazole* (=*3-Bromo-9*H-*carbazol-2-ol Acetate*; **5a**). White needles (hexane). M.p. 138–139°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.30 (br. *s*, H–N(9)); 7.82 (*s*, H–C(4)); 7.71 (*d*, *J* = 8.3, H–C(5)); 7.38 (*dd*, *J* = 1.9, 8.6, H–C(7)); 7.26 (*t*, *J* = 8.3, H–C(6)); 7.25 (*d*, *J* = 8.3, H–C(8)); 7.02 (*s*, H–C(1)); 2.47 (*s*, Me). ^{13}C-NMR ($CDCl_3$, 200 MHz): 170.6 (CO); 149.3 (C(2)); 140.5 (C(9a)); 140.0 (C(8a)); 128.1 (C(7)); 122.1 (C(4)); 122.8 (C(5)); 120.1 (C(4b)); 119.5 (C(4a)); 113.1 (C(8)); 112.2 (C(6)); 105.5 (C(3)); 104.0 (C(1)); 21.2 (Me). EI-MS (70 eV): 305 (12.5), 303 (10.3, M^+), 263 (67.3), 261 (67, $[M-CH_2{=}CO]^+$), 182 (100, $[M-CH_2{=}CO-Br]^+$), 154 (25.4), 127 (21.9). Anal. calc. for $C_{14}H_{10}BrNO_2$ (304.14): C 55.29, H 3.31, Br 26.27, N 4.61; found: C 55.19, H 3.29, Br 26.37, N 4.63.

*2-(Acetyloxy)-6-bromo-9*H-*carbazole* (=*6-Bromo-9*H-*carbazol-2-ol Acetate*; **5b**). White plates (hexane). M.p. 160–161°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.21 (br. *s*, H–N(9)); 7.95 (*d*, *J* = 2.1, H–C(5)); 7.75 (*d*, *J* = 8.8, H–C(4)); 7.45 (*dd*, *J* = 2.1, 8.3, H–C(7)); 7.17 (*d*, *J* = 8.3, H–C(8)); 7.04 (*d*, *J* = 2.4, H–C(1)); 6.87 (*dd*, *J* = 2.4, 8.8, H–C(3)); 2.40 (*s*, Me). ^{13}C-NMR ($CDCl_3$, 200 MHz): 170.6 (CO); 149.3 (C(2)); 140.5 (C(9a)); 139.0 (C(8a)); 128.1 (C(7)); 122.6 (C(4)); 120.8 (C(5)); 120.1 (C(4a)); 119.5 (C(4b)); 113.1 (C(8)); 112.2 (C(6)); 112.1 (C(1)); 103.9 (C(3)); 21.2 (Me). EI-MS (70 eV): 305 (8.5), 303 (9.3, M^+), 263 (57.3), 261 (56, $[M-CH_2{=}CO]^+$), 182 (100, $[M-CH_2{=}CO-Br]^+$), 154 (27.4), 127 (17.9). Anal. calc. for $C_{14}H_{10}BrNO_2$ (304.14): C 55.29, H 3.31, Br 26.27, N 4.61; found: C 55.25, H 3.28, Br 26.36, N 4.64.

*2-(Acetyloxy)-3,6-dibromo-9*H-*carbazole* (=*3,6-Dibromo-9*H-*carbazol-2-ol Acetate*; **5c**). White needles (hexane/AcOEt 9:1). M.p. 170°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.56 (br. *s*, H–N(9)); 7.71 (*d*, *J* = 1.8, H–C(5)); 7.60 (*s*, H–C(4)); 7.48 (*dd*, *J* = 1.8, 8.5, H–C(7)); 7.11 (*d*, *J* = 8.5, H–C(8)); 6.94 (*s*, H–C(1)); 2.47 (*s*, Me). ^{13}C-NMR ($CDCl_3$, 200 MHz): 168.6 (CO), 145.7 (C(2)); 139.4 (C(9a)); 139.2 (C(8a)); 128.5 (C(7)); 124.4 (C(4)); 123.1 (C(5)); 123.0 (C(4b)); 120.9 (C(4a)); 113.1 (C(8)); 111.2 (C(6)); 106.5 (C(1)); 105.7 (C(3)); 20.6 (Me). EI-MS (70 eV): 385 (13), 383 (26.5, M^+), 381 (12.5), 343 (32.4), 341 (65, $[M-CH_2{=}CO]^+$), 339 (31.7), 262 (95.3), 260 (100, $M-CH_2{=}CO-Br]^+$), 181 (25.3), 153 (12.3), 126 (9.8). Anal. calc. for $C_{14}H_9Br_2NO_2$ (383.04): C 43.90, H 2.37, Br 41.72, N 3.66; found: C 43.86, H 2.35, Br 41.82, N 3.69.

*6-Bromo-3-nitro-9*H-*carbazole* (**6a**). Yellow plates (hexane). M.p. 175°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 11.1 (br. *s*, H–N(9)); 8.83 (*d*, *J* = 2.1, H–C(4)); 8.22 (*dd*, *J* = 2.1, 8.4, H–C(2)); 8.13 (*d*, *J* = 2.3, H–C(5)); 7.46 (*dd*, *J* = 2.3, 8.1, H–C(6), H–C(7)); 7.37 (*d*, *J* = 8.4, H–C(1)); 7.28 (*d*, *J* = 8.1, H–C(8)). ^{13}C-NMR ($CDCl_3$, 200 MHz): 143.4 (C(3)); 140.1 (C(8a)); 139.6 (C(9a)); 129.6 (C(7)); 123.9 (C(5); 121.9 (C(4b)); 121.7 (C(2)); 121.1 (C(4b)); 118.0 (C(4)); 113.7 (C(8)); 112.3 (C(6)); 111.4 (C(1)). EI-MS (70 eV): 292 (100), 290 (76, M^+), 262 (20.3), 260 (19.0, $[M-NO]^+$), 246 (24.7), 244 (29.3, $[M-NO_2]^+$), 165 (46), 164 (31.9, $[M-NO_2-Br]^+$). Anal. calc. for $C_{12}H_7BrN_2O_2$ (291.10): C 49.51, H 2.42, Br 27.45, N 9.62; found: C 49.61, H 2.45, Br 27.38, N 9.58.

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Received February 14, 2006