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Received December 6, 2001

Iododerivatives of *N*-methylcarbazole (**1**), *N*-phenylcarbazole (**2**), *N*-benzylcarbazole (**3**), 2-methoxy-*N*-methylcarbazole (**4**) and 3-acetamido-*N*-ethylcarbazole (**5**) are synthesised. *N*-Iodosuccinimide (NIS) in tetrahydrofuran/H₂SO₄ (catalyst), a mixture of KIO₃ - KI - H₂SO₄ (catalyst) in ethanol and a mixture of KIO₃ - KI in glacial AcOH as iodinating agents have been used and their uses have been compared. The preparation, isolation and characterization of compounds **1a**, **1b**, **1c**, **1d**, **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **4c** and **5a** are reported (mp, t_R , R_F , ¹H-nmr, ¹³C-nmr, IR and ms). All of them are described for the first time except 3,6-diiodo-*N*-phenylcarbazole (**2b**). Semiempirical PM3 calculations have been performed to predict reactivity of *N*-substituted carbazoles and their iododerivatives. Theoretical and experimental results are discussed briefly.

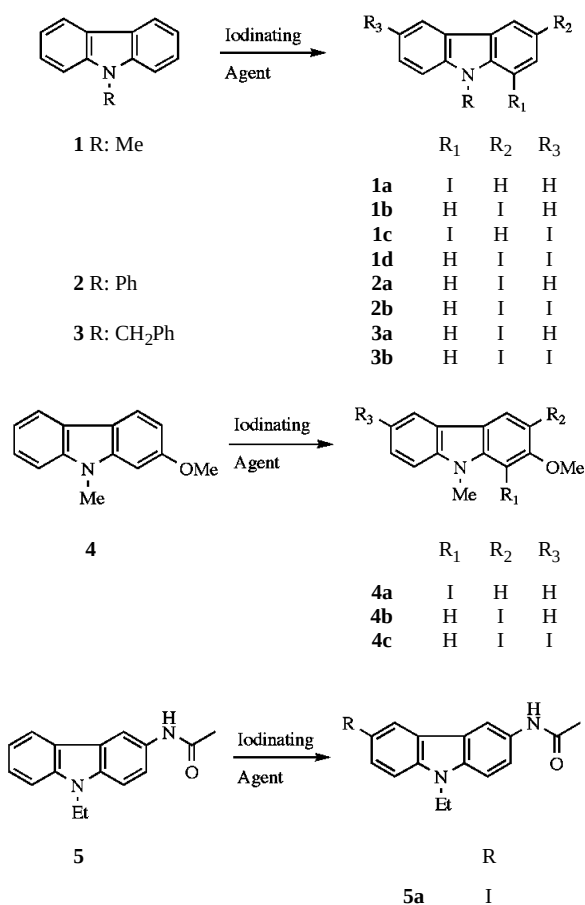
J. Heterocyclic Chem., **39**, 933(2002).

Introduction.

In our previous publication [1] we described the synthesis of five iododerivatives of carbazole and several new iodo derivatives of 2-hydroxy-, 2-acetoxy-, 3-bromo- and 3-nitrocarbazole. As we are interested in the study of photophysics and photochemistry of azacarbazoles [2-8], carbazoles [9,10], *N*-acetylcarbazole and *N*-benzoylcarbazole [11-13] and especially in the photoinduced electron transfer processes in which they can be involved, we decided to start the study of the photophysical properties of the iododerivatives of the *N*-substituted carbazoles. Thus, in the present work we report the synthesis, isolation and characterization of several *N*-substituted iodocarbazoles prepared by direct iodination of *N*-methyl (**1**), *N*-phenyl (**2**), *N*-benzyl (**3**), 2-methoxy-*N*-methyl (**4**) and 3-acetamido-*N*-ethylcarbazole (**5**) (Scheme 1: compounds **1a**, **1b**, **1c**, **1d**, **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **4c** and **5a**).

According to our knowledge, polymers containing carbazolyl moieties are good electron donors and possess outstanding electrical and photoelectrical properties [14 - 16]. It is also known that the presence of halogen in the polymer structure modifies their physical properties [17], and in particular, the presence of iodine in the polymer can modify the photophysical, and as a consequence, the photoelectrical properties of the polymer owing to the so called "heavy atom effect" [18].

In contrast to chlorination or bromination, the iodination of aromatic compounds is a mild reaction and generally requires some activating catalyst. Traditionally, the direct iodination reaction of aromatic compounds (benzenic, polynuclear benzenic rings and heterocycles) [19] were carried out with a mixture of KIO₃ or NaIO₄ and molecular iodine in ethanol in the presence of catalytic amounts of sulfuric acid or in glacial acetic acid, which is used as acid catalyst and solvent, at 70-100°. Other iodinating methods are peracetic acid, hydrogen peroxide (H₂O₂) and potassium permanganate (KMnO₄) as oxidizing agents to oxidize the molecular iodine in trifluoroacetic acid at room temperature or by warming the



system at 50°. Also, heavy metal ions such as Cu(II), Pb(IV), Sb(V), Co(III), Mn(IV) and Ce(IV) are used as oxidizing agents combined with alkaline iodide salts in the presence of 90% trifluoroacetic acid [19]. These iodinating methods are less commonly used because aromatic compounds with acid labile or oxidizable substituted groups (ester, amides, acyloxy, amines and alkyl) are easily hydrolyzed, protonated and/or oxidized under the above mentioned experimental conditions.

Recently, we described *N*-iodosuccinimide (NIS) in dichloromethane [1] as a convenient and mild iodinating agent providing mono, di and polyiodo compounds depending on the stoichiometry used.

The previously described iodination reaction of *N*-methylcarbazole with one equivalent of KIO_3/KI in the presence of acetic acid provided a mixture of 3-iodo-*N*-methylcarbazole (**1b**) and 3,6-diiodo-*N*-methylcarbazole (**1d**) which were characterized by their melting point and elemental analysis [20]. The same authors also described the preparation of compounds **1b** and **1d** by the action of methyl sulfate and potassium hydroxide on 3-iodocarbazoles and 3,6-diiodocarbazole, respectively [21].

3,6-Diiodo-*N*-phenylcarbazole (**2b**) was prepared by reacting *N*-phenylcarbazole (**2**) with two equivalents of a mixture of KIO_3/KI in the presence of acetic acid under reflux and it was characterized by its melting point, elemental analysis and ir spectra [22]. Although, Ambrose *et al.* [22] pointed out that the purity and the structure of 3,6-diiodo-*N*-phenylcarbazole (**2b**) was confirmed by ^1H -nmr spectroscopy the spectroscopical data were not reported.

As far as we know, the direct iodination of *N*-benzylcarbazole (**3**), 2-methoxy-*N*-methyl (**4**) and 3-acetamido-*N*-ethylcarbazole (**5**) has not been described. Furthermore, several iododerivatives of these carbazoles and those from carbazoles **1** and **2** have not been previously described.

In the present paper, we describe the preparation, isolation and characterization of several iodocarbazole derivatives obtained from *N*-substituted carbazoles (compounds **1**, **2**, **3**, **4** and **5**; see Scheme 1) by direct iodination using two different iodinating agents: i) KIO_3/KI in the presence of acid as catalyst and ii) NIS/THF/ H_2SO_4 (cat.). These iodinating systems are convenient as mild reagents for the selective preparation of mono- and diiodo-*N*-substituted carbazoles providing for the first time iodocarbazoles **1a**, **1c**, **2a**, **3a**, **3b**, **4a**, **4b**, **4c** and **5a** (see Scheme 1).

We also describe the use of several chromatographic methods (tlc, gc and column chromatography) in order to (i) follow the iodination reaction, (ii) determine the yields of the reactions and (iii) isolate for complete characterization (elemental analysis, R_f , t_R , mp, UV, ^1H -nmr, ^{13}C -nmr and ms) of the iododerivatives obtained.

Additionally, computational chemistry has been used to calculate the atomic charge density values. Those for the more relevant atoms are collected in Tables VI and they are used to discuss the reactivity of carbazoles **1-5**.

Results and Discussion.

In order to investigate the iodination reaction of *N*-substituted carbazoles **1-5**, we decided to carry out the reaction systematically and comparatively by using different iodinating reagents. Thus, KIO_3/KI in ethanol with catalytic amounts of concentrated sulfuric acid, or in glacial acetic acid as solvent-catalyst [20 - 22], and *N*-iodosuccin-

imide in tetrahydrofuran in the presence of catalytic amount of H_2SO_4 were used.

N-Methylcarbazole (**1**) was treated according to the general procedure described in Experimental with one to two equivalents of $\text{KIO}_3/\text{KI}/\text{H}_2\text{SO}_4$ (catalytic amount) in ethanol at 55° in order to prepare the iodocarbazole derivatives (Scheme I: **1a**, **1b**, **1c** and **1d**). The yields of the products were determined by gc after an appropriate time and the results are presented in Table I.

As it is shown in Table I (entry 1), this reaction provides a mixture of 3-iodo-*N*-methylcarbazole (**1b**) and 3,6-diiodo-*N*-methylcarbazole (**1d**) when one equivalent of the iodinating reagent was used. Also, in this reaction mixture 1,6-diiodo-*N*-methylcarbazole (**1c**) was detected as the minor product. We also performed the iodination reaction of compound **1** at lower temperature (room temperature) but selectivity on the product chemical yields was not observed. In this case, the reaction time became longer and the conversion of **1** was not improved (see Table I, entry 2). When two equivalents of iodinating agent were used (1:2 molar ratio), 3,6-diiodo-*N*-methylcarbazole (**1d**) was obtained as the main product and also compounds **1b** and **1c** were formed in significant amounts (see Table I, entry 3).

In our hands, the iodination reaction of *N*-methylcarbazole (**1**) provides a product distribution that is quite different from that previously reported [20]. The author only describes the formation of 3-iodo-*N*-methylcarbazole (**1b**) and 3,6-diiodo-*N*-methylcarbazole (**1d**) in the reaction mixture and these compounds were characterized by their melting point and elemental analysis.

The iodination reaction of **1** was also carried out with a mixture of KIO_3/KI in glacial acetic acid at 55° (see Table I, entries 4 and 5). As it is shown, the production of **1b** was fairly clean when one equivalent of the iodinating agent was used. The yield of compound **1d** was fairly improved by using two equivalents of the iodinated agent and higher conversion of the starting material was reached. Besides, in both reaction mixtures, compounds **1a** and **1c** were detected. It is noteworthy to mention that when acetic acid is used, both as solvent and acid catalyst, moniodination reaction preferably occurs using one or two equivalents of the reagent. Thus, compound **1b** is formed as the main product in both reaction mixtures.

In our previous publication [1] we described the use of *N*-iodosuccinimide (NIS) in dichloromethane, as a mild iodinating agent in the iodination reaction of carbazoles in neutral conditions. Taking into account these results, we decided to study the use of NIS for the iodination of *N*-substituted carbazoles. Thus, *N*-methylcarbazole (**1**) in CH_2Cl_2 with *N*-iodosuccinimide (1:1 molar ratio) was treated in the absence of light, at room temperature, during 2 hours. The gc analysis of the reaction mixture showed that 3-iodo-*N*-methylcarbazole (**1b**) was formed as the

only product in 12% yield (see Table I, entry 8). Besides, no improvement on the chemical yield of **1b** was observed when the reaction was left to stand for additional 7 hours. However, when the iodination reaction of *N*-methylcarbazole (**1**) was carried out with one equivalent of NIS in

duced the expected products, 3-iodo-*N*-phenyl (**2a**) and 3-iodo-*N*-benzylcarbazole (**3a**) respectively, in good yield (see Table II, entry 1 and Table III, entry 1). However, in both reaction mixtures significant amounts of the corresponding 3,6-diiodo-*N*-phenyl (**2b**) and 3,6-diiodo-*N*-ben-

Table I
Iodination of *N*-Methylcarbazole (**1**) by using Different Methods
Products (% Yield) [a]

Experiment	Method [b]	Carbazole:IA (molar ratio) [c]	Conversion (%)	1a	1b	1c	1d
1	(i)	1:1	94	-	83.1	2.0	8.8
2 [d]	(i)	1:1	95	-	84.0	2.1	7.5
3	(i)	1:2	100	-	3.4	1.5	95.1
4	(ii)	1:1	94.5	3.7	78.2	2.4	10.3
5	(ii)	1:2	97.6	0.6	59.4	2.4	35.2
6	(iii)	1:1	86.9	-	76.7	1.4	8.7
7	(iii)	1:2	100	-	18.4	1.9	79.7
8	(iv)	1:1	12	-	12	-	-

[a] Quantitative gc (ZB-5) analysis. Reaction time: 120 minutes; [b] Method: (i) KIO₃/KI/EtOH/H₂SO₄ (catalyst), T: 55°; (ii) KIO₃/KI/AcOH, T: 55°; (iii) *N*-Iodosuccinimide (NIS)/THF/H₂SO₄ (catalyst), T: 40°, (iv) *N*-Iodosuccinimide (NIS)/CH₂Cl₂, T: 25°; [c] *N*-Methylcarbazole to iodinating agent (IA) molar ratio; [d] Experiment at room temperature.

Table II
Iodination of *N*-Phenylcarbazole (**2**) by using Different Methods
Products (% Yield) [a]

Experiment	Method [b]	Carbazole:IA (molar ratio) [c]	Conversion (%)	2a	2b
1	(i)	1:1	88.3	80.3	7.9
2	(i)	1:2	100	0.8	99.2
3	(ii)	1:1	88.5	81.2	7.3
4	(ii)	1:2	100	68.8	31.0
5	(iii)	1:1	80.5	78.5	2
6	(iii)	1:2	99	46	53

[a] Quantitative gc (ZB-5) analysis. Reaction time: 300 minutes; [b] Method: (i) KIO₃/KI/EtOH/H₂SO₄ (catalyst), T: 55°; (ii) KIO₃/KI/AcOH, T: 55°; (iii) *N*-Iodosuccinimide (NIS)/THF/H₂SO₄ (catalyst), T: 40°; [c] *N*-Phenylcarbazole to iodinating agent (IA) molar ratio.

tetrahydrofurane in the presence of catalytic amount of H₂SO₄ at 40°, the product distribution changed dramatically and the chemical yields were improved (see Table I, entry 6). This reaction provides 3-iodo-*N*-methylcarbazole (**1b**) as the main product (76.7%) together with 1,6-diiodo-*N*-methylcarbazole (**1c**, 1.4%) and 3,6-diiodo-*N*-methylcarbazole (**1d**, 8.7%). When the iodination reaction of **1** was carried out with two equivalents of *N*-iodosuccinimide, production of 3,6-diiodo-*N*-methylcarbazole (**1d**) was higher (79.7%) but a significant amount of **1b** was also obtained. Compound **1c** was also detected in the reaction mixture (see Table I, entry 7).

N-Phenylcarbazole (**2**) and *N*-benzylcarbazole (**3**) are rather less reactive than *N*-methylcarbazole. Thus, the iodination reactions with a mixture of KIO₃/KI/H₂SO₄ in ethanol (1:1 molar ratio) were carried out at 55° during longer periods of time. Monoiodination of **2** and **3** pro-

Table III
Iodination of *N*-Benzylcarbazole (**3**) by using Different Methods
Products (% Yield) [a]

Experiment	Method [b]	Carbazole:IA (molar ratio) [c]	Conversion (%)	3a	3b
1	(i)	1:1	100	75.9	23.3
2	(i)	1:2	100	29.7	70.3
3	(ii)	1:1	77.7	74.4	3.3
4	(ii)	1:2	83.0	78.9	4.1
5	(iii)	1:1	82.7	79.1	3.6
6	(iii)	1:2	99.5	15.9	83.6

[a] Quantitative gc (ZB-5) analysis. Reaction time: 120 minutes; [b] Method: (i) KIO₃/KI/EtOH/H₂SO₄ (catalyst), T: 55°; (ii) KIO₃/KI/AcOH, T: 55°; (iii) *N*-Iodosuccinimide (NIS)/THF/H₂SO₄ (catalyst), T: 40°; [c] *N*-Benzylcarbazole to iodinating agent (IA) molar ratio.

duced the expected products, 3-iodo-*N*-phenyl (**2a**) and 3-iodo-*N*-benzylcarbazole (**3a**) respectively, in good yield (see Table II, entry 1 and Table III, entry 1). However, in both reaction mixtures significant amounts of the corresponding 3,6-diiodo-*N*-phenyl (**2b**) and 3,6-diiodo-*N*-ben-

phenylcarbazole (**2b**) was obtained in a high yield (99.2 %; see Table II, entry 2) while 3,6-diiodo-*N*-benzylcarbazole (**3b**) was formed in good yield (see Table III, entry 2) but a significant amount of compound **3a** was also detected in the reaction mixture. In all these iodinating reactions, a high conversion of the starting material was reached.

The iodination reactions of **2** and **3** were also carried out with a mixture of KIO_3/KI in glacial acetic acid at 55° and the results are shown in Table II, entry 3 and Table III, entry 3, respectively. As it is shown, the production of **2a** and **3a** was fairly clean. As it has been discussed previously, moniodination is the preferential reaction using both one and two equivalents of this reagent (see Table II, entry 4 and Table III, entry 4).

We also studied the iodination reaction of *N*-phenylcarbazole (**2**) and *N*-benzylcarbazole (**3**) with one and two equivalents of *N*-iodosuccinimide in THF doped with catalytic amount of sulfuric acid at 40° in the absence of light (see Tables II and III, entries 5 and 6, respectively). Thus, the production of 3-iodo-*N*-phenylcarbazole (**2a**) was fairly clean when one equivalent of NIS was used and 3,6-diiodo-*N*-phenylcarbazole (**2b**) was also detected in the reaction mixture. The same pattern of results was obtained with *N*-benzylcarbazole (**3**) in these conditions. When two equivalents of NIS were used, compounds **2a** and **2b** were formed in almost 1:1 molar ratio.

When *N*-benzylcarbazole (**3**) reacted with *N*-iodosuccinimide in a molar ratio 1:1 at 40°, again 3-iodo-*N*-benzylcarbazole (**3a**) was obtained as the main product together with a 3.6% yield of 3,6-diiodo-*N*-benzylcarbazole (**3b**) whereas the iodination reaction of **3** with two equivalents of NIS renders **3b** in 83.6% yield together with significant amount of compound **3a** (see Table III, entries 5 and 6). Comparing entries 2 and 6 in Table II, we conclude that compound **2b** is obtained in high yield (99.2%) when the iodinating mixture $\text{KIO}_3/\text{KI}/\text{EtOH}/\text{H}_2\text{SO}_4$ (catalyst) is used.

It is noteworthy to mention that in the iodination reaction of *N*-methylcarbazole, 1-iodo-*N*-methyl (**1a**) and 1,6-diiodo-*N*-methylcarbazole (**1c**) were formed in low yield

while, in the iodination reaction of *N*-phenyl and *N*-benzylcarbazole, neither 1-iodo nor 1,6-diiodo-*N*-substituted carbazoles were detected in the reaction mixtures. Comparing these results with those obtained when the iodination reaction of carbazole was performed with a mixture of $\text{NaIO}_4/\text{I}_2/\text{H}_2\text{SO}_4$ in ethanol [1], we conclude that the incoming electrophile (I^+) at the *ortho*-position of the carbazole moiety is dramatically diminished when a substituent group is attached to the heteroatom. This behavior is due to the presence of a bulky *N*-substituent such as methyl, phenyl and benzyl group in the carbazole moiety and, at the same time, to the high molecular volume of the electrophile (I^+). Therefore, a steric effect at the *ortho*-position of the carbazole moiety is operating in the electrophilic iodination reaction of *N*-substituted carbazole derivatives.

We also studied the iodination reaction of 2-methoxy-*N*-methylcarbazole (**4**) according to the general procedure described in the Experimental. The yields of the products obtained (gc) are presented in Table IV. As it is shown in this table (entry 1) the reaction conducted at 55° provided 3-iodo-2-methoxy-*N*-methylcarbazole (**4b**), together with significant amounts of 3,6-diiodo-2-methoxy-*N*-methylcarbazole (**4c**) and traces of 1-iodo-2-methoxy-*N*-methylcarbazole (**4a**) when one equivalent of iodinating agent ($\text{KIO}_3/\text{KI}/\text{H}^+$) was used. When two equivalents of the iodinating agent were used, 3,6-diiodo-2-methoxy-*N*-methylcarbazole (**4c**) was formed in a fairly good yield together with traces of **4a** and **4b** (see Table IV, entry 2) and a total consumption of the starting material was reached.

Simultaneously, we carried out the iodination reaction of **4** with KIO_3/KI in glacial acetic acid and the results are shown in Table IV (entries 3 and 4). Again, one equivalent of the iodinating agent provides a mixture of compounds **4b** and **4c** in almost a 9:1 molar ratio, while when two equivalents of the iodinating agent were used, similar product yields were obtained.

The iodination reactions of 2-methoxy-*N*-methylcarbazole (**4**) with one and two equivalents of *N*-iodosuccin-

Table IV
Iodination of 2-Methoxy-*N*-methylcarbazole (**4**) by using Different Methods
Products (% Yield) [a]

Experiment	Method [b]	Carbazole:IA	Conversion (molar ratio) [c]	4a (%)	4b	4c
1	(i)	1:1	99.8	0.9	69.0	29.9
2	(i)	1:2	100	1.2	0.6	98.0
3	(ii)	1:1	99.1	0.8	88.0	10.4
4	(ii)	1:2	99.1	0.9	81.1	17.1
5	(iii)	1:1	82.0	6.8	75.2	-
6	(iii)	1:2	99.4	1.1	28.8	69.5

[a] Quantitative gc (ZB-5) analysis. Reaction time: 120 minutes; [b] Method: (i) $\text{KIO}_3/\text{KI}/\text{EtOH}/\text{H}_2\text{SO}_4$ (catalyst), T: 55°; (ii) $\text{KIO}_3/\text{KI}/\text{AcOH}$, T: 55°; (iii) *N*-Iodosuccinimide (NIS)/THF/ H_2SO_4 (catalyst), T: 40°; [c] 2-Methoxy-*N*-methylcarbazole to iodinating agent (IA) molar ratio.

imide were also studied. As it is shown in Table IV (entries 5 and 6), the use of one equivalent of NIS as iodinating agent provides 3-iodo-2-methoxy-*N*-methylcarbazole (**4b**) in 75.2% yield together with 1-iodo-2-methoxy-*N*-methylcarbazole (**4a**). Any diiodo derivative (**4c**) was detected in the reaction mixture. When two equivalents of NIS were used, 3,6-diiodo-2-methoxy-*N*-methylcarbazole (**4c**) was formed in good yield together with significant amount of compound **4b**. Compound **4a** was also detected in the reaction mixture.

The iodination reaction of 3-acetamido-*N*-ethylcarbazole (**5**) with one equivalent of $\text{KIO}_3/\text{KI}/\text{H}_2\text{SO}_4$ in ethanol yielded 6-iodo-3-acetamido-*N*-ethylcarbazole (**5a**) as the sole product in 90.6% yield. When two equivalents of the iodinating agent were used, again the only product detected in the reaction mixture was **5a** in 100% yield (see Table V, entries 1 and 2). When the acid catalyst used in the iodination reaction of **5** was glacial acetic acid instead of sulfuric acid, similar results were obtained. Thus, the use of one or two equivalents of the iodinating agent (KIO_3/KI) in acetic acid gives as sole product **5a** in very high yield and the conversion of starting material is almost complete (see Table V, entries 3 and 4).

Finally, we studied the iodination reaction of 3-acetamido-*N*-ethylcarbazole (**5**) with one and two equivalents of *N*-iodosuccinimide and the results are shown in Table V (entries 5 and 6). As it is shown, 6-iodo-3-acetamido-*N*-ethylcarbazole (**5a**) was formed again as the sole product in 100% yield when one or two equivalents were used.

Furthermore, as it was pointed out above, all these reactions were monitored by gc in order to obtain additional information about the mechanism of the iodination reaction. The kinetic profiles obtained for the iodination reaction of **1** with one equivalent of the reagent, show that **1a** and **1b** are formed in parallel reactions. When two equivalents of the iodinating agent are used, **1a** and **1b** are the

primary products which in turn give 1,6-diiodo-*N*-methylcarbazole (**1c**) and 3,6-diiodo-*N*-methylcarbazole (**1d**), respectively, where **1d** is the main product of the iodination reaction of **1** (see Table I, entries 1 and 3). Following the kinetic profiles obtained for the iodination reaction of the *N*-substituted carbazoles (**2** – **5**), all of the mono and diiodo-*N*-substituted carbazoles are formed in parallel reactions.

The differential reactivity of the carbazoles **1** – **5** towards the electrophilic substitution iodination could be rationalized taking into account charge distribution. As it is known the static charge distribution is frequently used for interpreting and predicting chemical reactivity and it should indicate favorable sites for kinetic attack by incoming reagents. The net atomic charge values were calculated by using the semi empirical PM3 method as implemented in the version of the HyperChem 5.1 program [23] to obtain the optimized geometry of the *N*-substituted carbazoles and their iodo derivatives.

The static atomic charge density values calculated for compounds **1**, **2**, **3**, **4** and **5** and their iododerivatives are collected in Table VI. These *N*-substituted carbazoles (**1** – **5**) have the highest negative values localized at C-1, C-3, C-6 and C-8 and it would be expected that the incoming iodine cation (I^+) could preferentially attack these positions. It is worthwhile to point out that C-3 and C-6 have the highest negative charge density values compared to that of C-1 and C-8.

As it is shown in Table VI, the static charge values pattern of carbazoles **1** and **4** show the preferential electrophilic substitution positions, which are in agreement with the experimental results obtained. Besides, for carbazoles **2**, **3** and **5**, even though the highest negative charge density values are localized at C-1, C-3 and also at C-6, C-8, the experimental results obtained show a preferential *para*-substitution mechanism. These results can be explained taking into account the large volume of the iodine cation (I^+) and the bulky group (phenyl, benzyl and ethyl) attached to the nitrogen atom of the carbazole moiety. Both effects operate simultaneously and make the approach of the electrophile (I^+) difficult at the *orto*-position (1-C and 8-C) of the carbazole moiety. The difference in the DH_f calculated for each pair of iodo derivatives isomers (1-, 3-iododerivatives of carbazole and mono- and diiododerivatives obtained from compounds **1**-**5**, see Table VI) agree with the regioselectivity observed.

EXPERIMENTAL

Thin layer chromatography (tlc) analysis was performed with aluminum silica gel sheets (0.2 layer thickness, silica-gel 60 F254). Gas chromatography (gc) analysis was conducted with a Zebtron ZB-5 column (Crosslinked 5% Phenylpolysiloxane; 30m x 0.25mm x 0.50 mm; Capillary column). Mass spectra (ms)

Table V

Iodination of 3-Acetamido-*N*-ethylcarbazole (**5**) by using Different Methods
Products (% Yield) [a]

Experiment	Method [b]	Carbazole:IA (molar ratio) [c]	Conversion (%)	5a
1	(i)	1:1	90.6	90.6
2	(i)	1:2	100	100
3	(ii)	1:1	98.8	98.8
4	(ii)	1:2	100	100
5	(iii)	1:1	100	100
6	(iii)	1:2	100	100

[a] Quantitative gc (ZB-5) analysis. Reaction time: 120 minutes;
[b] Method: (i) $\text{KIO}_3/\text{KI}/\text{EtOH}/\text{H}_2\text{SO}_4$ (catalyst), T: 55°; (ii) $\text{KIO}_3/\text{KI}/\text{AcOH}$, T: 55°; (iii) *N*-Iodosuccinimide (NIS)/ THF / H_2SO_4 (catalyst), T: 40°; [c] 3-Acetamido-*N*-ethylcarbazole to iodinating agent (IA) molar ratio.

Table VI

Static Charge Distribution for *N*-Methylcarbazole (**1**), *N*-Phenylcarbazole (**2**), *N*-Benzylcarbazole (**3**), 2-Methoxy-*N*-methylcarbazole (**4**) and 3-Acetamido-*N*-ethylcarbazole (**5**) and DH_f for the Iododerivatives [a]

Compounds	1-C	2-C	3-C	Atom Number 4-C	5-C	6-C	7-C	8-C	DH_f [b]
1	-0.131	-0.073	-0.140	-0.040					
1a	-0.126	-0.072	-0.119	-0.052	-0.049	-0.124	-0.082	-0.104	81.26569
1b	-0.120	-0.054	-0.159	-0.017	-0.039	-0.135	-0.073	-0.120	74.73787
1c	-0.128	-0.069	-0.118	-0.049	-0.026	-0.150	-0.060	-0.100	102.51580
1d	-0.118	-0.052	-0.162	-0.015	-0.015	-0.159	-0.052	-0.116	97.57286
2	-0.177	-0.085	-0.126	-0.048					
2a	-0.113	-0.044	-0.153	-0.024	-0.046	-0.124	-0.083	-0.116	109.89489[c]
2b	-0.112	-0.062	-0.155	-0.022					131.43211[d]
3	-0.113	-0.081	-0.129	-0.048					
3a	-0.114	-0.060	-0.153	-0.024	-0.045	-0.128	-0.078	-0.112	100.71176[e]
3b	-0.113	-0.057	-0.154	-0.021	-0.022	-0.153	-0.057	-0.108	121.92529[f]
4	-0.212	0.119	-0.174	-0.007	-0.047	-0.134	-0.080	-0.120	
4a	-0.212	0.148	-0.182	-0.006	-0.046	-0.130	-0.081	-0.113	47.82892
4b	-0.214	0.142	-0.212	0.017	-0.046	-0.131	-0.080	-0.117	40.04039
4c	-0.195	0.137	-0.207	0.011	-0.031	-0.147	-0.065	-0.100	61.23724[g]
5	-0.099	-0.084	-0.110	-0.073	-0.046	-0.126	-0.078	-0.110	
5a	-0.098	-0.082	-0.108	-0.070	-0.022	-0.155	-0.056	-0.107	22.63604[h]

[a] Calculations were performed using PM3 method [23]; [b] DH_f in kcal/mol; DH_f for 1-iodocarbazole: 79.72475 kcal/mol and for 3-iodocarbazole: 75.83298 kcal/mol; [c] DH_f for 1-iodo-*N*-phenylcarbazole: 115.05375 kcal/mol; [d] DH_f for 1,6-diiodo-*N*-phenylcarbazole: 159.19018 kcal/mol; [e] DH_f for 1-iodo-*N*-benzylcarbazole: 109.94786 kcal/mol; [f] DH_f for 1,6-diiodo-*N*-benzylcarbazole: 131.17812 kcal/mol; [g] DH_f for 1,6-diiodo-2-methoxy-*N*-ethylcarbazole: 75.22029 kcal/mol and for 1,3-diiodo-2-methoxy-*N*-ethylcarbazole: 80.99334 kcal/mol; [h] DH_f for 1-iodo-3(*N*-acetylamine)-*N*-ethylcarbazole: 31.03466 kcal/mol.

were obtained under electron impact (70 eV). The ratios m/z and the relative intensities are reported. Products were isolated by preparative thick layer chromatography (PLC Merck Plates, 20x20 cm, silica gel 60 F254, 2 mm thickness) and column chromatography (Aldrich silica gel 200-400 mesh 60Å). Pure hexane and hexane-ethyl acetate mixtures were used as eluent. Melting points are uncorrected. ^1H - and ^{13}C -nmr spectra were run in deuteriochloroform at 200 MHz. Chemical shifts are reported in ppm values, using tetramethylsilane as internal standard. ^{13}C -nmr assignments were confirmed by using DEPT pulse sequence.

Dichloromethane, tetrahydrofurane, benzene, acetic acid, ethanol, hexane, ethyl acetate and other reagents used were analytical grade. Solvents were freshly distilled and dried before using. Carbazole, *N*-methylcarbazole, *N*-phenylcarbazole, 3-amino-*N*-ethylcarbazole and *N*-iodosuccinimide were purchased from Aldrich. 2-Hydroxycarbazole was purchased from Aldrich and was recrystallized from ethanol before use. 2-Methoxy-*N*-methylcarbazole [24], *N*-benzylcarbazole [25] and 3-acetamido-*N*-ethylcarbazole [26] were prepared according to the procedure described in the literature.

General Procedure for the Iodination Reaction of *N*-Methylcarbazole (**1**) with KIO_3/KI /Catalytic Acid Systems.

To a stirred solution of *N*-methylcarbazole (**1**) (100 mg, 0.55 mmoles) in ethanol (20 mL) solid sodium iodate (0.15 to 0.30 mmole depending on the stoichiometry used) and potassium iodine previously grinded (0.28 to 0.56 mmole depending on the stoichiometry used) were added. Then concentrated sulfuric acid (42 nL to 1.68 mL depending on the stoichiometry used, d: 1.85 g/mL) was added drop wise. The reaction was stirred for an appropriate time in the absence of light at 55° until the tlc and gc indicated that it was completed. All of these reactions were carried out

under normal (air) atmosphere. The reaction mixture was neutralized with sodium bisulphite, extracted with dichloromethane (3 x 15 mL) and washed with water (3 x 20 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated *in vacuo* to give a brownish solid residue. The residue was separated by column chromatography (silica gel-hexane-ethyl acetate mixtures) to give (**1a**), (**1b**), (**1c**) and (**1d**). According to the experimental conditions used the percentage yield of the products obtained are different as can be seen in Table I (see Results and Discussion). Besides, these set of reaction were performed in glacial acetic acid instead of ethanol, because it works as solvent and acid catalyst simultaneously.

1-Iodo-*N*-methylcarbazole (**1a**).

This compound was obtained as white needles (hexane), mp 95-96 °; ^1H -nmr (deuteriochloroform): d 8.05 (d, 1 H, 5-H, $J = 7.8$ Hz), 7.90 (dd, 1 H, 4-H, $J = 1.8$ and 8.0 Hz), 7.45 (dd, 1 H, 2-H, $J = 1.8$ and 8.0 Hz), 7.43-7.38 (m, 2 H, 6- and 7-H), 7.25 (dd, 8-H, $J = 2.0$ and 7.8 Hz), 7.15 (dd, 1 H, 3-H, $J = 8.0$ and 8.0 Hz), 3.80 ppm (s, 3 H, CH_3); ms: m/z 307 (26), 306 (M^+ , 100), 179 (19), 178 (24), 166 (25), 139 (15).

Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{NI}$: C, 50.84; H, 3.28; N, 4.56; I, 41.32. Found: C, 50.80; H, 3.30; N, 4.54; I, 41.28.

3-Iodo-*N*-methylcarbazole (**1b**).

This compound was obtained as white needles (hexane), mp 67-69°; ^1H -nmr (deuteriochloroform): d 8.40 (d, 1 H, 4-H, $J = 1.9$ Hz), 8.04 (d, 1H, 5-H, $J = 7.8$ Hz), 7.72 (dd, 1 H, 2-H, $J = 1.9$ and 8.5 Hz), 7.52 (dd, 1 H, 7-H, $J = 7.8$ and 7.8 Hz), 7.39 (dd, 1 H, 8-H, $J = 2.3$ and 7.8 Hz), 7.27 (ddd, 1 H, 6-H, $J = 2.3$, 7.8 and 7.8 Hz), 7.17 (d, 1 H, 1-H, $J = 8.5$ Hz), 3.82 ppm (s, 3 H, CH_3); ^{13}C -nmr (deuteriochloroform): d 140.9, 140.0, 133.8, 129.0, 126.5, 125.3,

121.5, 120.6, 119.4, 110.6, 108.7, 81.5, 29.0 ppm; ms: m/z 307 (15), 306 (M^+ , 100), 179 (19), 178 (35), 166 (42), 139 (18).

Anal. Calcd. for $C_{13}H_{10}NI$: C, 50.84; H, 3.28; N, 4.56; I, 41.32. Found: C, 51.00; H, 3.25; N, 4.52; I, 41.28.

1,6-Diiodo-*N*-methylcarbazole (**1c**).

This compound was obtained as white needles (hexane), mp 120–121°; 1H -nmr (deuteriochloroform): δ 8.00 (d, 1 H, 5-H, J = 2.0 Hz), 7.95 (d, 1 H, 4-H, J = 8.0 Hz), 7.45 (d, 1 H, 2-H, J = 8.0 Hz), 7.30 (d, 1 H, 8-H, J = 7.8 Hz), 7.25 (dd, 1 H, 7-H, J = 2.0 and 7.8 Hz), 7.10 (dd, 1 H, 3-H, J = 8.0 and 8.0 Hz), 3.79 ppm (s, 3 H, CH_3); ms: m/z 434 (13), 433 (M^+ , 100), 307 (6), 306 (21), 247 (31), 245 (33), 216 (17), 179 (19), 178 (24), 166 (25), 139 (15).

Anal. Calcd. for $C_{13}H_9NI_2$: C, 36.06; H, 2.09; N, 3.23; I, 58.61. Found: C, 36.10; H, 2.01; N, 3.24; I, 58.31.

3,6-Diiodo-*N*-methylcarbazole (**1d**).

This compound was obtained as white needles (hexane), mp 187°; 1H -nmr (deuteriochloroform): δ 8.32 (d, 2 H, 4- and 5-H, J = 1.6 Hz), 7.72 (dd, 2H, 2- and 7-H, J = 1.6 and 7.0 Hz), 7.16 (d, 2 H, 1- and 8-H, J = 7.0 Hz), 3.79 ppm (s, 3 H, CH_3); ^{13}C -nmr (deuteriochloroform): δ 140.1, 134.6, 129.3, 123.9, 110.7, 81.8, 29.3 ppm; ms: m/z 434 (10), 433 (M^+ , 100), 307 (6), 306 (21), 179 (29), 178 (34), 166 (55), 139 (15).

Anal. Calcd. for $C_{13}H_9NI_2$: C, 36.06; H, 2.09; N, 3.23; I, 58.61. Found: C, 36.00; H, 2.11; N, 3.21; I, 58.34.

Iodination Reaction of *N*-Phenylcarbazole (**2**) with KIO_3/KI /Catalytic Acid Systems.

The iodination reaction of *N*-phenylcarbazole (**2**) was performed according to the general procedure described above. The brownish solid residue was separated by preparative thick layer chromatography (silica gel; hexane-benzene (90:10)) to give two crystalline products **2a** and **2b**. The percentage yields of the products obtained are presented in Table II (see Result and Discussion).

3-Iodo-*N*-phenylcarbazole (**2a**).

This compound was obtained as white needles (hexane), mp 107–109°; 1H -nmr (deuteriochloroform): δ 8.43 (dd, 1 H, 5-H, J = 1.6 and 8.0 Hz), 8.09 (d, 1 H, 4-H, J = 2.0 Hz), 7.70–7.63 (m, 2 H, 2- and 7-H), 7.53 (m, 2 H, 10- and 14-H), 7.41–7.38 (m, 3 H, 11-, 12- and 13-H), 7.31 (dd, 1 H, 6-H, J = 8.0 and 8.0 Hz), 7.18 (d, 1 H, 8-H, J = 8.8 Hz), 7.15 ppm (d, 1 H, 1-H, J = 8.4 Hz); ^{13}C -nmr (deuteriochloroform): δ 141.1, 140.2, 137.4, 134.3, 130.2, 129.3, 127.9, 127.1, 126.8, 126.0, 124.5, 120.6, 120.5, 111.9, 110.0, 82.3 ppm; ms: m/z 369 (26), 368 (M^+ , 100), 242 (10), 241 (7), 239 (15), 165 (3), 164 (13), 138 (4).

Anal. Calcd. for $C_{18}H_{12}NI$: C, 58.56; H, 3.28; N, 3.79; I, 34.37. Found: C, 58.50; H, 3.30; N, 3.80; I, 34.35.

3,6-Diiodo-*N*-phenylcarbazole (**2b**).

This compound was obtained as white needles (hexane), mp 179–180° ([22] 179–182°); 1H -nmr (deuteriochloroform): δ 8.40 (d, 2 H, 4- and 5-H, J = 1.5 Hz), 7.67 (dd, 2 H, 2- and 7-H, J = 1.5 and 8.8 Hz), 7.60 (m, 2 H, 10- and 14-H), 7.55–7.45 (m, 3 H, 11-, 12- and 13-H), 7.15 ppm (d, 2 H, 1- and 8-H, J = 8.8 Hz); ^{13}C -nmr (deuteriochloroform): δ 140.1, 136.8, 135.0, 130.2, 129.4, 128.2, 127.0, 124.5, 112.0, 83.1 ppm; ms: m/z 496 (23), 495 (M^+ , 100), 368 (27), 242 (10), 241 (7), 239 (15), 164 (13), 138 (4).

Anal. Calcd. for $C_{18}H_{11}NI_2$: C, 43.67; H, 2.24; N, 2.83; I, 51.26. Found: C, 43.65; H, 2.27; N, 2.80; I, 51.22.

Iodination Reaction of *N*-Benzylcarbazole (**3**) with *N*-Iodosuccinimide.

The iodination reaction of *N*-benzylcarbazole (**3**) was performed according to the general procedure described above. The brownish solid residue was separated by preparative thin layer chromatography (silica gel; hexane-benzene (90:10)) to give two crystalline products **3a** and **3b**. The percentage yields of the products obtained are presented in Table III (see Result and Discussion).

3-Iodo-*N*-benzylcarbazole (**3a**).

This compound was obtained as white needles (hexane), mp 107–109°; 1H -nmr (deuteriochloroform): δ 8.44 (dd, 1 H, 5-H, J = 1.6 and 8.0 Hz), 8.07 (d, 1 H, 4-H, J = 1.9), 7.70–7.63 (m, 2 H, 2- and 7-H), 7.53 (m, 2 H, 10- and 14-H), 7.32–7.24 (m, 3 H, 11-, 12- and 13-H), 7.31 (dd, 1 H, 6-H, J = 8.0 and 8.0 Hz), 7.18 (d, 1 H, 8-H, J = 8.8 Hz), 7.15 (d, 1 H, 1-H, J = 8.4 Hz), 5.50 ppm (s, 2 H, CH_2); ^{13}C -nmr (deuteriochloroform): δ 140.7, 139.9, 136.8, 134.1, 129.5, 129.3, 127.7, 126.6, 126.4, 125.6, 121.9, 120.6, 119.8, 111.1, 109.2, 81.9, 46.5 ppm; ms: m/z 384 (5), 383 (M^+ , 22), 292 (1), 257 (8), 167 (16), 164 (5), 91 (100).

Anal. Calcd. for $C_{19}H_{14}NI$: C, 59.55; H, 3.68; N, 3.65; I, 33.11. Found: C, 59.53; H, 3.64; N, 3.67; I, 33.10.

3,6-Diiodo-*N*-benzylcarbazole (**3b**).

This compound was obtained as white needles (hexane), mp 169–172°; 1H -nmr (deuteriochloroform): δ 8.38 (d, 2 H, 4- and 5-H, J = 1.5 Hz), 7.70 (dd, 2 H, 2- and 7-H, J = 1.5 and 8.8 Hz), 7.55 (m, 2 H, 10- and 14-H), 7.28–7.23 (m, 3 H, 11-, 12- and 13-H), 7.15 ppm (d, 2 H, 1- and 8-H, J = 8.8 Hz); ^{13}C -nmr (deuteriochloroform): δ 139.3, 137.1, 134.3, 129.3, 128.3, 127.3, 126.5, 123.5, 112.1, 82.5, 45.6 ppm; ms: m/z 509 (M^+ , 1), 384 (5), 383 (26), 292 (2), 254 (4), 166 (2), 164 (7), 91 (100).

Anal. Calcd. for $C_{19}H_{13}NI_2$: C, 44.82; H, 2.57; N, 2.75; I, 49.85. Found: C, 44.80; H, 2.50; N, 2.78; I, 49.82.

Iodination Reaction of 2-Methoxy-*N*-methylcarbazole (**4**) with KIO_3/KI /Catalytic Acid Systems.

The iodination reaction of 2-methoxy-*N*-methylcarbazole (**4**) was performed according to the general procedure described above. The brownish solid residue was separated by column chromatography (silica gel-hexane-ethyl acetate mixtures) to give three crystalline products **4a**, **4b** and **4c**. The percentage yields of the products obtained are presented in Table IV (see Result and Discussion).

1-Iodo-2-methoxy-*N*-methylcarbazole (**4a**).

This compound was obtained as white needles (hexane), mp 130°; 1H -nmr (deuteriochloroform): δ 7.99 (dd, 1 H, 5-H, J = 2.3 and 7.8 Hz), 7.87 (d, 1 H, 4-H, J = 8.4 Hz), 7.38 (m, 2 H, 6- and 7-H), 7.19 (d, 1 H, 8-H, J = 7.0 Hz), 6.89 (d, 1 H, 3-H, J = 8.4 Hz), 4.09 (s, 3 H, CH_3N), 3.95 ppm (s, 3 H, CH_3O); ^{13}C -nmr (deuteriochloroform): δ 159.2, 150.1, 139.6, 125.7, 124.6, 119.4, 119.1, 119.0, 117.8, 108.4, 104.7, 79.1, 56.7, 29.2 ppm; ms: m/z 338 (10), 337 (M^+ , 100), 322 (20), 294 (13), 208 (3), 196 (5), 195 (39), 180 (26), 167 (34), 152 (27), 139 (10).

Anal. Calcd. for $C_{14}H_{12}NOI$: C, 49.87; H, 3.59; N, 4.15; I, 37.64. Found: C, 49.85; H, 3.60; N, 4.12; I, 37.65.

3-Iodo-2-methoxy-*N*-methylcarbazole (4b).

This compound was obtained as white needles (hexane), mp 160-163°; ¹H-nmr (deuteriochloroform): δ 8.43 (s, 1 H, 4-H), 7.95 (d, 1 H, 5-H, J = 7.7 Hz), 7.43-7.38 (m, 2 H, 6- and 7-H), 7.23 (dd, 1 H, 8-H, J = 2.0 and 7.6 Hz), 6.83 (s, 1 H, 1-H), 4.01 (s, 1 H, CH₃O), 3.81 ppm (s, 1 H, CH₃N); ¹³C-nmr (deuteriochloroform): δ 156.5, 142.3, 141.0, 130.6, 125.0, 121.7, 119.6, 119.5, 118.8, 108.4, 91.5, 75.2, 56.6, 29.1 ppm; ms: m/z 338 (15), 337 (M⁺, 100), 322 (21), 294 (19), 208 (3), 196 (6), 195 (42), 180 (26), 167 (30), 152 (24), 139 (12).

Anal. Calcd. for C₁₄H₁₂NOI: C, 49.87; H, 3.59; N, 4.15; I, 37.64. Found: C, 49.82; H, 3.57; N, 4.12; I, 37.66.

3,6-Diiodo-2-methoxy-*N*-methylcarbazole (4c).

This compound was obtained as white needles (hexane), mp 198°; ¹H-nmr (deuteriochloroform): δ 8.33 (s, 1 H, 4-H), 8.20 (d, 1 H, 5-H, J = 1.1 Hz), 7.62 (dd, 1 H, 7-H, J = 1.1 and 8.8 Hz), 7.09 (d, 1 H, 8-H, J = 8.8 Hz), 6.74 (s, 1 H, 1-H), 3.99 (s, 1 H, CH₃O), 3.74 ppm (s, 1 H, CH₃N); ¹³C-nmr (deuteriochloroform): δ 153.1, 141.8, 139.4, 134.4, 130.9, 128.4, 124.1, 117.0, 110.4, 91.3, 82.0, 75.2, 56.7, 29.2 ppm; ms: m/z 464 (12), 463 (M⁺, 100), 338 (15), 322 (23), 294 (15), 208 (8), 196 (6), 195 (52), 180 (26), 167 (34), 152 (24), 139 (12).

Anal. Calcd. for C₁₄H₁₁NOI₂: C, 36.31; H, 2.39; N, 3.02; I, 54.81. Found: C, 36.30; H, 2.35; N, 3.04; I, 54.79.

Iodination Reaction of 3-Acetamido-*N*-ethylcarbazole (5) with KIO₃/KI/Catalytic Acid Systems.

The iodination reaction of 3-acetamido-*N*-methylcarbazole (5) was performed according to the general procedure described above. The yellowish solid residue was separated by column chromatography (silica gel-hexane-ethyl acetate mixtures) to give a crystalline product **5a**. The percentage yield of the product obtained is presented in Table V (see Result and Discussion).

3-Acetamido-6-iodo-*N*-ethylcarbazole (5a).

This compound was obtained as white needles (hexane), mp 175°; ¹H-nmr (deuteriochloroform): δ 8.32 (d, 1 H, 5-H, J = 1.5 Hz), 8.18 (d, 1 H, 4-H, J = 1.5 Hz), 7.66 (dd, 1 H, 2-H, J = 1.5 and 8.8 Hz), 7.54 (dd, 1 H, 7-H, J = 1.5 and 8.8 Hz), 7.31 (d, 1 H, 1-H, J = 8.8 Hz), 7.16 (d, 1 H, 8-H, J = 8.8 Hz), 4.28 (q, 2 H, CH₂), 2.19 (s, 3 H, CH₃CONH), 1.36 ppm (t, 3 H, CH₃); ¹³C-nmr (deuteriochloroform): δ 169.7, 139.4, 137.0, 133.8, 130.4, 129.2, 125.2, 121.5, 120.3, 112.8, 110.5, 108.5, 80.7, 37.5, 23.4, 13.4 ppm; ms: m/z 370 (19), 369 (M⁺, 100), 243 (6), 242 (30), 241 (45), 240 (14), 213 (3), 164 (6), 121 (7), 51 (20).

Anal. Calcd. for C₁₆H₁₅N₂OI: C, 50.81; H, 4.00; N, 7.41; I, 33.55. Found: C, 50.79; H, 3.99; N, 7.43; I, 33.52.

General Procedure for the Iodination Reaction of *N*-Methylcarbazole (1) with *N*-Iodosuccinimide in Tetrahydrofuran.

To a stirred solution of *N*-methylcarbazole (**1**) (100 mg, 0.55 mmole) in tetrahydrofuran (10 mL) solid *N*-iodosuccinimide (0.55 mmole to 1.10 mmole depending on the stoichiometry used) was added. Then, concentrated sulfuric acid (42 mL; d: 1.85 g/mL) was carefully added. The reaction was stirred for an appropriate time in the absence of light at 40° until the tlc and gc indicated that it was completed. All of these reactions were carried out under normal (air) atmosphere. After the reaction mixture was neutralized with sodium hydroxide, the work-up was similar to that previously described for the reaction with KIO₃/KI/

catalytic acid systems. The product yields obtained in different experimental conditions are shown in Table I, entries 6 and 7 (see Results and Discussion).

Iodination Reaction of Carbazoles 2 - 5 with *N*-Iodosuccinimide.

The iodination reaction of carbazoles **2** - **5** with *N*-iodosuccinimide was performed according to the general procedure described above. The percentage yields of the products obtained are shown in Tables II, III, IV and V (entries 5 and 6), respectively (see Results and Discussion).

Iodination Reaction of *N*-Methylcarbazole (1) with *N*-Iodosuccinimide in Dichloromethane.

To a stirred solution of *N*-methylcarbazole (**1**) (100 mg, 0.55 mmole) in dichloromethane (10 mL) solid *N*-iodosuccinimide (0.55 mmole) was added. The reaction was stirred for an appropriate time in the absence of light at room temperature until the tlc and gc indicated that it was completed. This reaction was carried out under normal (air) atmosphere. The reaction mixture was evaporated *in vacuo* to give a brownish solid residue. The residue was separated by column chromatography (silica gel-hexane-ethyl acetate mixtures) to give (**1b**) and recovered starting material (**1**). The percentage yield of the product obtained is shown in Table I, entry 8 (see Results and Discussion).

Calculations.

The ground-state geometry and heat of formation, static charge distribution for predicting chemical reactivity of carbazoles **1** - **5** and iodocarbazoles were calculated by using the semiempirical parametrized PM3 method as implemented in version of the HyperChem program [23]. This method has proven to be effective in studies on molecules containing heteroatoms, compared with other methods such as MINDO/3 or MNDO.

Acknowledgment.

Partial financial support from UBA and CONICET is gratefully acknowledged. Authors are also grateful to Dr. H. Nonami (College of Agriculture, Ehime University, Japan) for HyperChem Suite for professionals release 5.1 program and Dr. M. A. Ponce for nmr spectra. S. M. Bonesi and R. Erra-Balsells are research members of CONICET.

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