

Halogenating and Nitrating Activity of Reagents Based on Sodium Nitrate and Alkali Metal Halides in Acetic Acid

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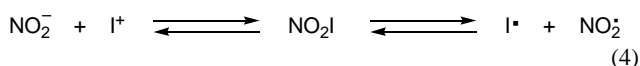
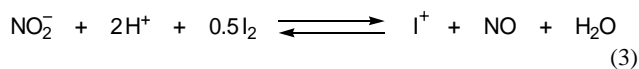
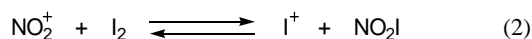
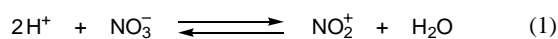
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Abstract—Alkali metal halides NaF, KCl, and KBr sharply enhance the nitrating activity of sodium nitrate in acetic acid with respect to 9-methylcarbazole. In the presence of KI and KBr, both nitration and halogenation of the substrate occurs, while KCl and NaF promote only the nitration process. The results may be interpreted in terms of formation of the corresponding nitryl halides XNO_2 ($X = F, Cl, Br, I$) whose structure and reactivity were examined in the framework of the density functional theory (DFT B3LYP/3-21G*).

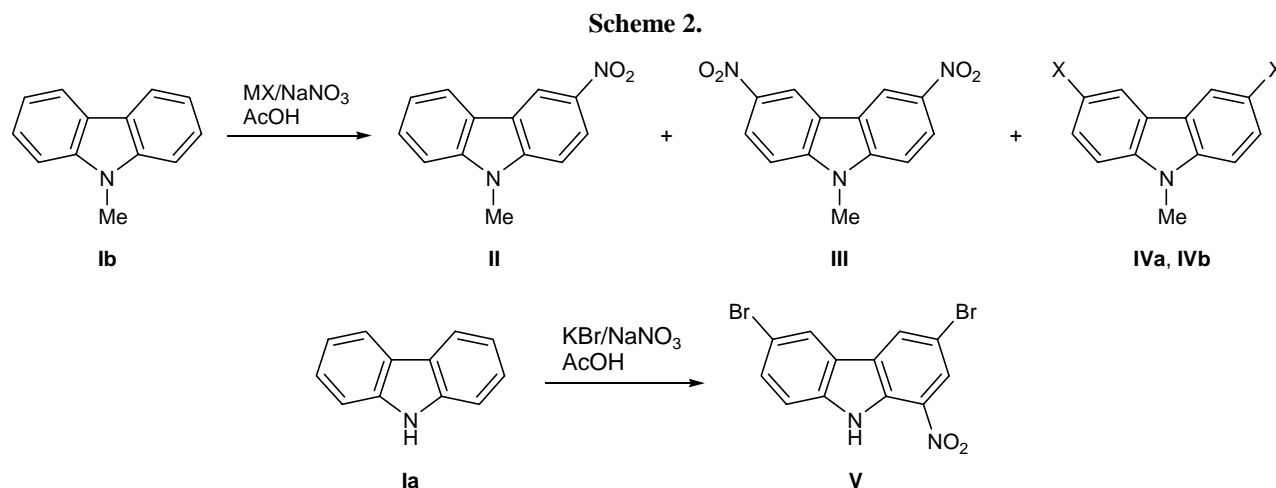
We previously showed that iodine in acetic acid in the presence of alkali metal nitrates acts as a mild iodinating agent toward some 9-alkylcarbazoles and activated arenes [1]. On the other hand, KI, as well as molecular iodine, in a mixture with nitrates reacts with alkynes to give the corresponding α -iodo- β -nitroalkenes [2]. The mechanism of action of these reagents is not clear, though we presumed in [3, 4] that a series of redox reactions between I_2 and NO_3^- in acetic acid gives rise to unstable nitryl iodide which, depending on the substrate nature, can act as both electrophilic and radical species (Scheme 1). It was presumed that carbazoles and arenes undergo typical electrophilic iodination and that in the presence of acetylenes radical addition of INO_2 at the triple bond occurs [1–4].

Scheme 1.



Taking into account that reagents on the basis of nitrates, halogens, and halides are attractive for organic synthesis due to their accessibility, mild action, and safety, we believed it reasonable to continue studies on elucidating the mechanism of action of these reagents and extending the scope of their application. In the present work we examined the behavior of sodium nitrate in the presence of alkali metal halides (KI, KBr, KCl, and NaF) with respect to carbazole (**Ia**) and 9-methylcarbazole (**Ib**) as typical π -excessive heterocycles possessing enhanced reactivity in electrophilic substitution reactions which are not accompanied by side processes [5].

Table 1 contains the results of reactions of $NaNO_3$ with 9-methylcarbazole (**Ib**) in acetic acid in the presence and in the absence of alkali metal halides. In the absence of the latter, partial nitration of compound **Ib** occurs to afford a mixture of 3-nitro- and 3,6-dinitrocarbazoles **II** and **III** (Scheme 2). Addition of KCl and NaF sharply increases the nitrating power, while KI and KBr promote not only nitration but also halogenation to give, respectively, 3,6-dibromo- and 3,6-diiodocarbazoles **IVa** and **IVb**. In the reaction with $KBr/NaNO_3$, the halogenation process predominates at room temperature, and this system may be used as



a convenient mild brominating agent: the preparative yield of compound **IVa** exceeds 80%. Nitrocarbazoles **II** and **III** are formed in appreciable amounts only at

Table 1. Reaction of 9-methylcarbazole (**Ib**) (0.5 mmol) with NaNO₃ in acetic acid in the presence and in the absence of alkali metal halides (MX)

Run no.	MX (mmol)	NaNO ₃ (mmol)	Time, h	Temp., °C	Yield, ^a %		
					II	III	IV
1	–	2.0	30	20	5	5	
2	–	2.0	15	85	37	45	
3	NaF (1.0)	2.0	1.5	85	18	46	
4	KCl (1.0)	2.0	1	85	40	16	
5	KBr (1.0)	2.0	20	10	4	3	70
6	KBr (1.0)	2.0	20	20	3	2	73
7	KBr (2.0)	1.0	20	20	7	5	67
8	KBr (2.0)	1.0	30	20	8	6	84
9	KBr (3.0)	–	30	20	0	0	0
10	KBr (2.0)	1	10	85	30	11	41
11	KBr (1.0)	1	10	85	23	11	19
12	KBr (1.0)	2	6	85	33	39	24
13	KI (2.0)	1	20	30	0	0	0
14	KI (2.0)	1	20	40	0	0	0
15	KI (2.0)	1.5	30	30	0	0	0
16	KI (1.0)	1	20	60	19	28	5
17	KI (1.0)	2	16	60	25	39	8
18	KI (1.0)	2	10	85	27	43	14
19	KI (1.0)	3	10	85	23	56	19
20	KI (1.0)	2	5	100	14	51	35

^a Yields of products isolated by column chromatography.

85°C and in the presence of increased amount of sodium nitrate (Table 1).

Carbazole (**Ia**) readily reacts with KBr/NaNO₃ (ratio 2:1) at 25°C to give 3,6-dibromo-1-nitrocarbazole (**V**) in 76% yield (unoptimized). Undoubtedly, the first stage of the process is bromination to give 3,6-dibromocarbazole, for the nitration of **Ia** with a number of reagents occurs preferentially at position 3, while 1-nitrocarbazole is frequently formed by rearrangement of such intermediates as 9-nitroso- or 9-nitrocarbazoles [5].

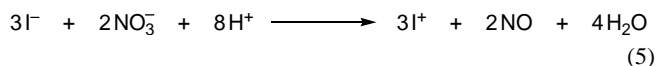
The most surprising were the results of the reaction of methylcarbazole **Ib** with KI/NaNO₃. The substrate remained unchanged below 40°C, indicating that KI clearly inhibits the nitrating activity of NaNO₃ at moderate temperatures (cf. run nos. 1 and 13–16, Table 1). Moreover, compound **Ib** readily undergoes iodination with the system I₂/NaNO₃/AcOH even at room temperature [1, 4], whereas iodination by the action of KI/NaNO₃ to give compound **IVb** begins only at a much higher temperature and is accompanied by nitration as the predominant process which does not occur in the reaction with I₂/NaNO₃.

We have found that the loss of iodinating power by the system KI/NaNO₃/AcOH is observed not only with respect to substrate **Ib** but is general. Even such a reactive substrate as anisole, which is readily iodinated with I₂/NaNO₃/AcOH (4-iodoanisole is formed in 92% in 4 h at 40°C [1]), remains almost intact in a mixture of KI, NaNO₃, and AcOH at room temperature; in 15 h at 40°C, the yield of 4-iodoanisole is as low as 20%. In addition, we observed liberation of iodine and NO₂ from solutions of KI and NaNO₃ in

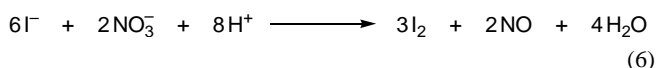
acetic acid at 20°C both in the absence and in the presence of compound **Ib**, i.e., the system $I_2/NaNO_3$ was reconstituted; however, no iodination of the substrate occurred. Therefore, we can conclude that, contrary to Scheme 1, iodide ion itself possesses a weak iodinating power and inhibits iodination by the action of $I_2/NaNO_3$.

The reasons for the lack of fluorination and chlorination of 9-methylcarbazole **Ib** in the systems $NaNO_3/NaF$ and $NaNO_3/KCl$ are quite obvious. These are high redox potentials of fluoride and chloride ions [6] and hence their inability to undergo oxidation under the above conditions. On the other hand, electrophilic iodination of arenes with iodine or iodide ion is usually promoted by a number of nitrogen-containing oxidants, e.g., $I_2/H_2SO_4/HNO_3$ (Tronov–Novikov system) [7], $I_2/NaNO_2/CF_3COOH$ [8], $I_2/NO_2/H_2SO_4$ [9], $NH_4I/NO^+BF_4^-/H^+$ [10], and $KI/H_2SO_4/HNO_3/O_2$ [11]. It is important that strongly acidic medium is necessary to reveal high electrophilic activity of iodine. According to [10], the iodination of anisole with the system $NH_4I/NO^+BF_4^-$ in CF_3COOH is complete in 1–2 h, while in $AcOH$ the conversion is only 1%.

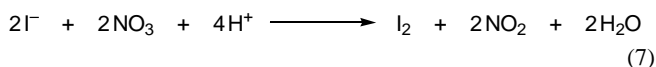
Electrophilic iodine I^+ should be generated by the reaction sequence $2I^- \rightarrow I_2 \rightarrow 2I^+$ as a result of thermodynamically possible redox reactions (5)–(9):



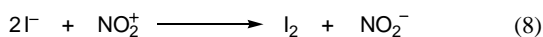
$$\varphi(I^-/I^+) = 0.76 \text{ V}, \varphi(NO_3^-/NO) = 0.96 \text{ V} [6], \\ E_0 \text{ (electromotive force)} = 0.2 \text{ V}, \Delta G = -11.8 \text{ kJ/mol};$$



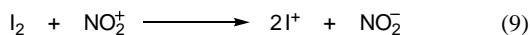
$$\varphi(I^-/I_2) = 0.54 \text{ V} [6], E_0 = 0.42 \text{ V}, \Delta G = -243.1 \text{ kJ/mol};$$



$$\varphi(NO_3^-/NO_2) = 0.803 \text{ V} [6], E_0 = 0.043 \text{ V}, \\ \Delta G = -16.6 \text{ kJ/mol};$$



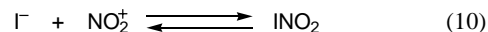
$$\varphi(NO_2^-/NO_2^+) = 1.5 \text{ V} [11], E_0 = 0.96 \text{ V}, \\ \Delta G = -370.56 \text{ kJ/mol};$$



$$\varphi(I_2/I^+) = 1.06 \text{ V} [6], E_0 = 0.44 \text{ V}, \\ \Delta G = -154.4 \text{ kJ/mol}.$$

Direct oxidation of iodide ion to electrophilic I^+ species [reaction (5)] can occur only in strongly acidic

media [11], i.e., it is impossible under our conditions. Liberation of elementary iodine according to reactions (6)–(8) was observed experimentally (see above). A reasonable interpretation of the weak iodinating ability of $KI/NaNO_3$ may be the following. When the initial concentration of iodide ions is high (which is the main difference from the system $I_2/NaNO_3$), its direct reaction with nitronium cation to give nityl iodide (NO_2I) prevails provided that the latter does not exhibit pronounced electrophilic activity.

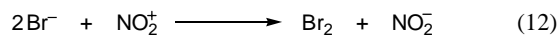


In other words, iodide ion binds the oxidant thus strongly reducing the concentration of electrophilic iodine formed as a result of redox processes with participation of I_2 . Binding of nitronium ions with iodide ions may be responsible for some inhibition by KI of the nitration of 9-methylcarbazole (**Ib**) at low temperatures (Table 1).

Undoubtedly, ionic reaction like (10) should also occur with other halides. To verify this assumption we determined the amount of N_2O_4 evolved from solutions of $NaNO_3$ in acetic acid into gas phase using the Griss reagent according to the procedure described in [12] (Table 2). It is clearly seen that the amount of liberated N_2O_4 decreases in the presence of NaF and KCl and that it strongly increases in the presence of I_2 , KI , and KBr . More than 10-fold reduction of the amount of N_2O_4 in the presence of KCl and NaF confirms the assumption that nitronium cation is bound with halide ion, giving rise to stable nityl halides XNO_2 ($X = F, Cl$). Oxidation of chloride and fluoride ions via reactions (5)–(9) is impossible due to their high redox potentials [6]. On the other hand, bromide ion, like iodide ion, should be oxidized to bromine cation or molecular bromine as a result of the following thermodynamically possible reactions:



$$\varphi(Br^-/Br^+) = 1.2 \text{ V}, \varphi(NO_2^-/NO_2^+) = 1.5 \text{ V} [11], \\ E_0 = 0.3 \text{ V}, \Delta G = -57.9 \text{ kJ/mol};$$



$$\varphi(Br^-/Br_2) = 1.09 \text{ V} [11], E_0 = 0.41 \text{ V}, \\ \Delta G = -77.2 \text{ kJ/mol}.$$

Thus the sharp increase of the fraction of N_2O_4 in the gas phase in the presence of I_2 , KI , and KBr (Table 2) provides an experimental proof for the occurrence of redox reactions (5)–(9), (11), and (12).

Table 2. Effect of I₂ (0.5 mmol) and alkali metal halides MX (1 mmol) on the amount of NO₂ released into the gas phase from solutions of NaNO₃ (2 mmol) in acetic acid (5 ml) at 85°C

Additive	Time, h	NO ₂ (mmol)
–	1	0.04
–	5	0.33
NaF	1	0.019
KCl	1	0.008
KCl	5	0.008
KBr	1	0.57
I ₂	1	0.38
I ₂	5	1.26
KI	1	0.53

Table 3. Lengths of the X–N bond in nitril halides NO₂X, charges on the halogen and nitrogen atoms (q_X , q_N), differences between these charges ($\Delta q = q_N - q_X$), and dipole moments (μ) of the X–N bonds, calculated by the B3LYP/3-21G* method

X	d_{X-N} , nm	q_X	q_N	Δq	μ_{X-N} , D	X–N bond polarization, %
F	1.507	–0.167	0.575	0.742	1.012	55, N → F
Cl	1.935	–0.026	0.398	0.424	0.510	58, N → Cl
Br	2.032	0.076	0.345	0.269	1.180	62, N ← Br
I	2.244	0.155	0.289	0.134	2.320	66, N ← I

In order to obtain an additional support to the presumed weak electrophilic iodination ability of nitril iodide and elucidate its origin, we performed quantum-chemical calculations of a series of nitril halides XNO₂ (X = F, Cl, Br, I) with geometry optimization in terms of the PM3 semiempirical method and density functional theory (B3LYP/3-21G*). The results given in Table 3 may be of general interest for the chemistry of nitril halides, taking into account that nitril fluoride and nitril chloride are used in practice and that nitril bromide and nitril iodide are postulated as intermediates in a number of reactions which are important for organic synthesis [13].

As might be expected on the basis of the electronegativities, the calculated electron density on the halogen atoms in nitril halides decreases in going from fluorine to iodine. However, the charge on the nitrogen atom decreases in parallel. As a result, the difference in the electron densities (Δq) on the halogen and

nitrogen atoms also decreases in the series F > Cl > Br ≫ I. For comparison, we calculated by the same procedure the charge on the iodine atom in hypoiodous acid IOH and obtained a q_I value of 0.355 which may be regarded as an additional evidence for the low electrophilicity of iodine in nitril iodide. The maximal apparent polarity and polarization of the I–N bond in nitril iodide are determined primarily by its maximal length.

Thermochemical calculations by the two methods (Tables 4, 5) indicate considerably greater probability of homolytic rather than heterolytic dissociation of the X–N bond in nitril halides, which is most clearly seen for nitril iodide (halogen cations X⁺ were calculated in the singlet state). We used the PM3 semiempirical procedure, for it allows direct comparison of the calculated enthalpies of formation ΔH of nitril halides and their dissociation products with the available experimental data [14]. As follows from the data in Table 4, a satisfactory agreement between the theoretical and experimental data is observed. In keeping with the ΔH values, the stability of nitril halides decreases in the series F > Cl > Br > I (Table 4). In fact, nitril fluoride and nitril chloride are known stable compounds; the lifetime of nitril bromide is 10 s [15]; and the formation of INO₂ was only postulated in reactions of iodine with nitrites or with N₂O₄ [16, 17].

Naturally, ionic decomposition products are stabilized to some extent due to solvation, but the differences in ΔH and ΔG for homolytic and heterolytic dissociation of the X–N bond are too large to be compensated by solvation effects. It should be also kept in mind that the most probable way of decomposition of nitril halides is heterolytic dissociation of the X–N bond with formation of the corresponding halide ions; however, we did not consider this process, for it implies trivial reversibility of the formation of XNO₂.

Comparison of KI/NaNO₃ and I₂/NaNO₃ reveals no appreciable difference between these reagents in the iodination–nitration of alkynes [1, 3]; however, they exhibit strongly different reactivities in electrophilic iodination. Our present results indicating intermediate formation of NO₂I in the system KI/NaNO₃ and predominantly radical reactivity of nitril iodide independently confirm the previous assumption that iodination–nitration of alkynes follows a radical mechanism [1, 3].

On the whole, our results do not refute Scheme 1 completely, but they show that processes involving KI

Table 4. Enthalpies of formation of nityl halides NO_2X and ionic and radical dissociation products and heats of the corresponding dissociation processes, calculated by the PM3 semiempirical method (kJ/mol)^a

X	Enthalpies of formation ΔH_f		Heats of dissociation ΔH	
	NO_2X	dissociation products	$\text{NO}_2\text{X} \rightarrow \text{X}^\cdot + \text{NO}_2^\cdot$	$\text{NO}_2\text{X} \rightarrow \text{X}^+ + \text{NO}_2^-$
F	-107.36 ^b (-108.87 [14])	F [·] 78.95, F ⁺ 1718.41	182.21	1645.98
Cl	-54.43 (12.17 [14])	Cl [·] 121.29, Cl ⁺ 1182.73	171.54	1057.38
Br	-42.01	Br [·] 111.88, Br ⁺ 1258.25	149.74	1120.52
I	36.02	I [·] 106.73 (106.86 [14]) I ⁺ 1187.13 (1122.44 [14])	66.57	971.31

^a Experimental data are given in parentheses.^b Enthalpies of formation ΔH_f of NO_2^\cdot and NO_2^- , calculated by the same procedure, are 4.14 and -179.79 kJ/mol, respectively.**Table 5.** Gibbs energies ΔG of nityl halides NO_2X , their ionic and radical dissociation products, and the corresponding dissociation processes, calculated by the B3LYP/3-21G* method^a

X	ΔG , a.u.		ΔG , kJ/mol	
	NO_2X	dissociation products	$\text{NO}_2\text{X} \rightarrow \text{X}^\cdot + \text{NO}_2^\cdot$	$\text{NO}_2\text{X} \rightarrow \text{X}^+ + \text{NO}_2^-$
F	-303.1824	F [·] -99.1970, F ⁺ -98.4416	167.94	2065.59
Cl	-662.0226	Cl [·] -458.0667, Cl ⁺ -457.5092	90.03	1468.83
Br	-2765.9628	Br [·] -2562.0055, Br ⁺ -2561.5067	94.22	1318.46
I	-7094.5699	I [·] -6890.6220, I ⁺ -6890.1812	69.53	1141.60

^a The Gibbs energies ΔG of NO_2^\cdot and NO_2^- , calculated by the same procedure, are -203.9214 and -203.9537 a.u., respectively.

and alkali metal nitrates in acetic acid are considerably more diverse than it seemed previously. Clearly, the contribution of acid-base equilibria is at least no less than the contribution of redox reactions, and all processes leading to formation of nityl iodide as intermediate reduce the electrophilic activity of iodine but enhance its radical reactivity. The iodinating ability of the system $\text{I}_2/\text{NO}_3/\text{AcOH}$ [1] originates from the presence of electrophilic iodine (I^+) in the form of acetyl hypoiodite CH_3COOI and I_3^+ .

It should be noted that the examined alkali metal halides not only enhance the nitrating potency of sodium nitrate but also affect the regioselectivity of the nitration in different ways. The difference is seen most clearly by comparing NaF and KCl (Table 1). Sodium fluoride ensures mainly formation of dinitrocarbazole **III**, while in the presence of potassium chloride mononitro derivative **II** is formed as the major product. The nitration results in the presence of KBr and KI are masked by concurrent halogenation: nevertheless, the formation of mononitro derivative predominates when KBr is present in excess with respect to NaNO_3

or their ratio is equimolar. Only with excess NaNO_3 , as well as in the absence of alkali metal halides, the fraction of dinitrocarbazole **III** sharply increases and becomes prevailing (run no. 12, Table 1). Addition of KI gives rise mainly to dinitrocarbazole **III**, regardless of the reactant ratio.

The above differences in the selectivity of nitration are consistent with intermediate formation of nityl halides and with their nitrating power series expected on the basis of the calculated electronic structure parameters (Table 3). The electrophilicity of the nitro group in nityl halides decreases in the series $\text{F} \gg \text{Cl} > \text{Br} \gg \text{I}$. The highest electrophilicity of nityl fluoride predetermines its poor selectivity which is comparable with the selectivity of nitronium cation (run nos. 2 and 3, Table 1). Relatively low electrophilicity of the nitro group in nityl chloride and nityl bromide should lead to reduced nitrating ability, especially with respect to deactivated mononitrocarbazole **II**. Correspondingly, inversion in the nitration selectivity in the presence of excess NaNO_3 over KBr (run no. 12, Table 1) indicates some contribution of "free" nitronium cation.

Presumably, the electrophilicity of nitril iodide is so weak that the nitration occurs by the action of nitronium cation and nitrogen oxides arising from homolytic dissociation of the I–N bond.

EXPERIMENTAL

The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates. Silica gel L 40/100 μm (Chemapol) was used for column chromatography. Elemental analysis was performed on an E.A. 1108 CHNS-O instrument. The melting points were determined on a Boetius device. The NMR spectra were recorded on a Bruker AC-200 spectrometer in chloroform-*d* using TMS as internal reference. The amount of NO_2 evolved from solutions of sodium nitrate in acetic acid was determined by standard procedure based on NO_2 adsorption by a film sorbent placed in ST 212 tubes, according to GU 25-1110-039-82 [12]; the procedure includes photometric determination of NO_2^- ion (formed from NO_2 and desorbed into an aqueous solution) via formation of azo dye with the Griss reagent. Products **II**, **III**, **IVa**, and **IVb** were identified by comparing their spectral parameters and physical constants with those of authentic samples [5].

Quantum-chemical calculations were performed with the aid of GAUSSIAN 98W software [18]. The geometric parameters were optimized, and the electronic structures were calculated, in terms of the density functional theory in the natural bond orbital approximation using B3 Becke exchange functional [19] and Lee–Yang–Parr correlation functional [20] (B3LYP NBO); the 3-21G* standard basis set included all electrons and allowed calculations to be performed for molecules containing iodine atoms.

Reaction of 9-methylcarbazole (Ib) with KI– NaNO_3 in acetic acid. A mixture of 2 mmol of NaNO_3 , 5 ml of acetic acid, 1 mmol of 9-methylcarbazole (**Ib**), and 1 mmol of KI was stirred for 10 h at 85°C. It was then poured into 70 ml of a 10% solution of $\text{Na}_2\text{S}_2\text{O}_3$, and the precipitate was filtered off, dried, and subjected to column chromatography. Elution with hexane afforded 3,6-diiodo-9-methylcarbazole (**IVb**), yield 27%, mp 179–181°C [1]; subsequent elution with hexane–benzene (1:2) gave 3-nitro-9-methylcarbazole (**II**), yield 43%, mp 165–166°C [21], and 3,6-dinitro-9-methylcarbazole (**III**), yield 14%, mp 265–267°C [22].

3,6-Dibromo-1-nitrocarbazole (V). A mixture of 0.5 mmol of carbazole (**Ia**), 5 ml of acetic acid, 2 mmol of KBr, and 1 mmol of NaNO_3 was stirred for 20 h at 25°C. It was then poured into 70 ml of a 10% solution of $\text{Na}_2\text{S}_2\text{O}_3$, and the precipitate was filtered off, dried, and subjected to column chromatography on silica gel using hexane as eluent. Yield 76%, mp 171–173°C (from EtOH). ^1H NMR spectrum (CDCl_3), δ , ppm: 7.13 s (1H, 8-H), 7.52 m (4H, 2-H, 4-H, 5-H, 7-H), 8.45 s (1H, NH). Found, %: C 40.1; H 1.59; Br 44.01; N 7.46. $\text{C}_{12}\text{H}_6\text{Br}_2\text{N}_2\text{O}_2$. Calculated, %: C 38.95; H 1.63; Br 43.19; N 7.57.

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