Synthesis and Properties of 3-Nitrosocarbazole

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The synthesis of 3-nitrosocarbazole (I) by the Fischer-Hepp rearrangement of 9-nitrosocarbazole has been described. The resistance of I to oxidation provides evidence that it cannot be the intermediate in the conversion of 9-nitrosocarbazole to the *C*-nitro compounds. It has also been shown that I and its derivatives cannot be synthesized by the action nitrosyl chloride on carbazoles. Methylation of I yields 9-methyl-3-nitrosocarbazole, 9,9'-dimethyl-3-azocarbazole and 9,9'-dimethyl-3-azoxycarbazole as the main products. The mechanism of this disproportionation process has been proposed. The spectral data of I are given.

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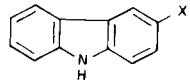
The title compound has not been described as yet although it was mentioned, in an erroneous context, for the first time as early as 1902 [1]. Drake *et al.* postulated existence of 3-nitrosocarbazole derivatives as the intermediates in the conversion of 1-substituted 9-nitrosocarbazoles to the corresponding 3- or 6-nitro compounds [2]. The first attempts to prepare 3-nitrosocarbazole were done by Shishkina in 1972 but the conclusions given in the paper [3] were in considerable doubt. In my hands the Shishkina's procedures gave different results.

The Fischer-Hepp rearrangement of 9-nitrosocarbazole was performed in acetic acid medium with the use of a large excess (14 equivalents) of concentrated hydrochloric acid. The crude product was extracted with benzene in order to remove the unreacted substrate and purified by crystallization. 3-Nitrosocarbazole (I) was obtained in 50-60% yield as green needles melting at 197-199° with decomposition. Vacuum sublimation gave dark green rods (brown in the transparent light) mp 202-204° dec.

The mass spectrum of 3-nitrosocarbazole consists of four significant signals: the molecular ion gives the abundant peak at m/e 196 (65.7), direct loss of the oxygen atom gives rise to the peak at m/e 180 (8.6); m/e 166 $(M\text{-}NO)^+$ is the base peak in the spectrum and the last intense signal is the doublet at m/e 140 (15.1) and 139 (41.7) which is observed in the spectra of several carbazole derivatives.

In the infrared spectrum of crystalline 3-nitrosocarbazole (in potassium bromide) the strong bands at 1340 and 1390 cm^{-1} are indicative of the presence of the nitroso group in the *cis*-dimeric form. In the region 1488-1513 cm^{-1} only skeletal vibrations characteristic of 3-substituted carbazole system are observed. The strong band at 1512 cm^{-1} assigned to the stretching vibration of the monomeric nitroso group occurs in the spectra of *N*-alkyl-3-nitrosocarbazoles. 9-Unsubstituted carbazole derivatives give a sharp and strong band in the 3400 cm^{-1} region. The frequency of the N-H stretching vibration is influenced with the electron accepting substituents:



νNH (potassium bromide)	3420	3410	3395	3345	3190	3160-3220
X	-H	-CL, Br	-N=N-	$-NO_2$	$-NMe_3^+$	-NO

Very broad and shifted towards lower wave numbers signal in the spectrum of 3-nitrosocarbazole indicates the presence of strong intermolecular hydrogen bonds. Dilute solutions of 3-nitrosocarbazole in benzene and carbon tetrachloride give the band assigned to N-H at 3420 and 3480 cm^{-1} respectively, while in dioxane the absorption is observed at 3245 cm^{-1} and is shifted gradually to 3275 cm^{-1} when the concentration increases.

The electronic spectra of 3-nitrosocarbazole (I) and its 9-alkyl derivatives consists of four bands characteristic of simple derivatives of carbazole, although strongly shifted. The bathochromic shift and hyperchromic effect increase with the wave length. The additional fifth band ($n \rightarrow \pi^*$) indicates that diluted alcoholic solutions contain I in the monomeric form.

Table I

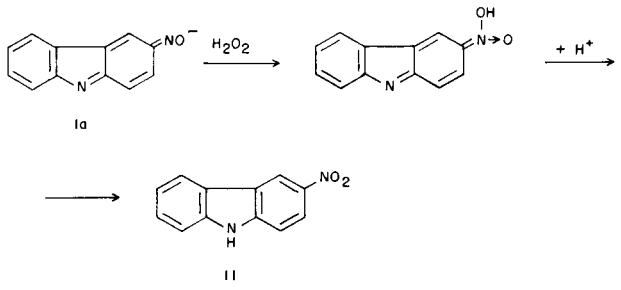
UV Spectra of 3-Nitroso and 3-Nitrocarbazole, λ max (ε)

	in Ethanol		in 0.1 *N* potassium hydroxide solution (90% aq ethanol)	
Band	I	II	I	II
β	235 (54,000)	231 (50,000)		
ϱ	285 (34,000)	281 (26,700)	291 (15,800)	298 (18,300)
α	318 (18,700)	307 (19,800)	336 (14,500)	336 (12,500)
τ	398 (18,000)	366 (9,800)	467 (17,200)	474 (10,500)
ϱ	699 (70)			

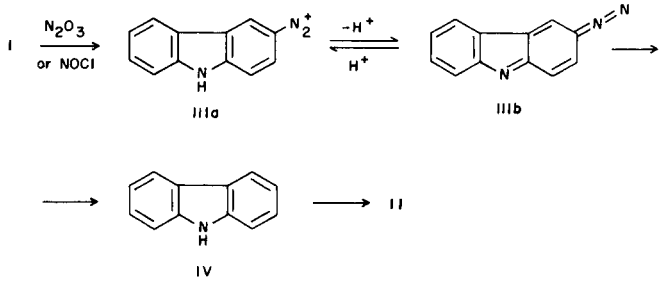
The spectra of I and 3-nitrocarbazole (II) differs markedly in the long wave region while Shishkina reported them as "undistinguishable". Considering the mp of the compound described as "3-nitrosocarbazole" (162-164°)

[3] it seems most likely that it is 3-nitrocarbazole-1-nitrocarbazole 1:1 complex [4]. The spectra of I and II registered in the alkaline solutions are very similar. The strong absorption of the chinoid anion Ia in the 470 nm region is observed as the deep purple colour of alkaline I solutions.

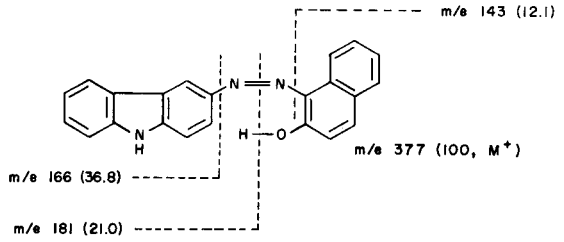
An interesting feature of I is its resistance to oxidation. Potassium permanganate in acetic acid medium does not oxidize 3-nitrosocarbazole while chromic oxide causes destruction of the carbazole rings. The attempted auto-oxidation was performed by passing a stream of air through the boiling solution of I in xylene for 4 hours. The substrate was recovered unchanged, no trace of II could be detected in the reaction mixture. The oxidation with peracetic acid in boiling acetic acid solution also failed. Much more sensitive to oxidation is the 3-nitrosocarbazolate anion Ia. In the alkaline aqueous acetone solution I was smoothly oxidized with hydrogen peroxide to the corresponding nitro compound.



The action of nitrous acid (sodium nitrite in acetic acid solution) was supposed to be the only example of the oxidation process of I to II but further experiments demonstrated that it was a complex reaction. Probably it follows the scheme:



In the presence of sodium acetate the oxidation does not occur even at elevated temperature. Addition of hydrochloric acid (1 equivalent) to the mixture of I and sodium nitrite (4 equivalents, used as a 4 *M* aqueous solution) in acetic acid medium gives rise to the rapid conversion of I to IIIa. The intermediate III has not been isolated but when the reaction has been performed at room temperature and the mixture poured into a cold alkaline solution of 2-naphthol the azo compound has been formed. 1-(Carbazolyl-3-azo)-1-naphthol was isolated in 68% yield as maroon needles, mp 275-277°. The spectral data are in agreement with the structure designed below:

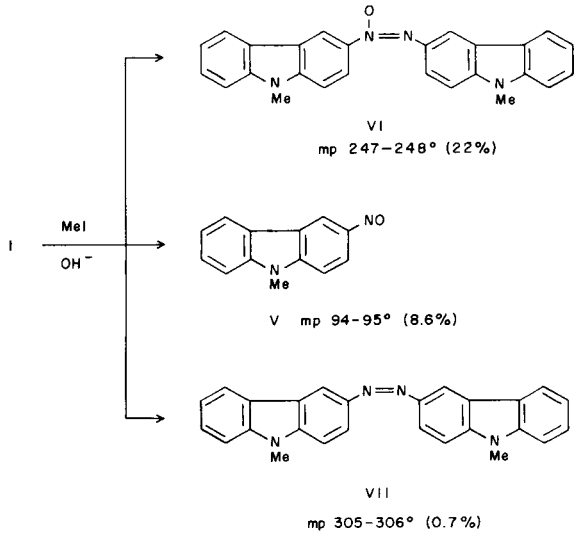


The coupling with 2-naphthol provided evidence that a diazo compound (probably IIIb) is formed also in the absence of hydrochloric acid. A free radical mechanism of the transformation III→II seems to be unacceptable considering the reaction condition as well as the S_N1 mechanism however, this is well known that 3-hydroxycarbazole cannot be obtained from the disazotised amine [5,6]. Probably expulsion of the nitrogen molecule from IIIa results in the loss of the pyrrole proton and formation of the intermediate of a carbone or diradical character which is not susceptible to nucleophilic attack. This reactive species yields carbazole and oligomers. Hence formation of III is the result of the reaction of carbazole and nitric acid generated from nitrous oxide in the disproportionation process. Indeed, II disazotised with sodium nitrite and hydrochloric acid yields carbazole if the mixture is treated with urea before boiling.

In conclusion it can be stated that the reaction of carbazole derivatives with nitrosyl chloride as described in the patents [7,1] cannot provide nitroso compounds. Contrary to the results reported by Drake *et al.* [2] it was found that nitrocarbazoles cannot be formed directly from the corresponding nitroso compounds neither in the auto-oxidation process nor by the action of an excess of nitrous acid.

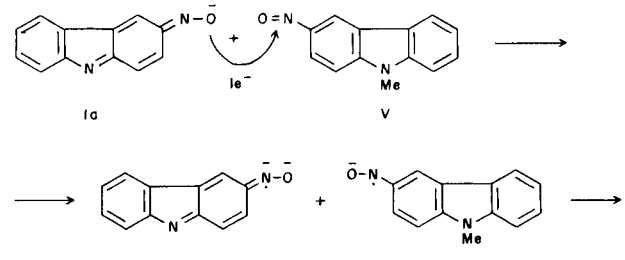
Several experiments have been carried out with the objective of preparing some simple derivatives of 3-nitrosocarbazole. The procedure commonly used for the synthesis of 3-nitro-9-methylcarbazole [8,9] was adapted to the 3-nitroso-9-methylcarbazole (V) preparation. The crude product (brown tar) was extracted with boiling toluene. The solution when cooled to −20° deposited orange needles, mp 247-248°. The structure of 9,9'-dimethyl-3-azoxycarbazole (VI) was assigned to the compound on the basis of the spectral data. The same compound has been obtained from 3-nitro-9-methylcarbazole *via* bimolecular reduction with lithium aluminium hydride and subsequent oxidation as described in the paper [10].

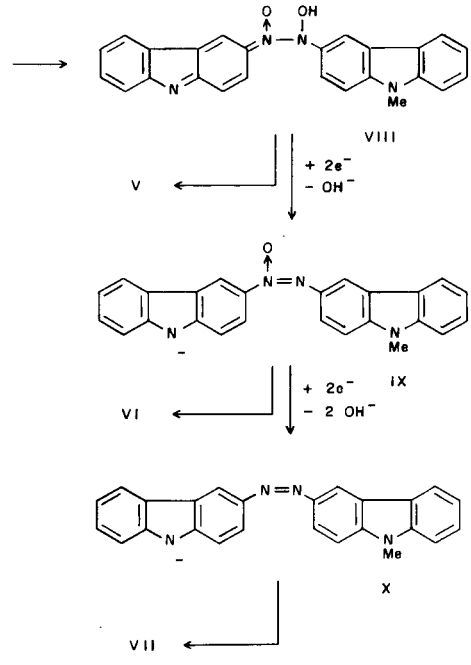
When the crude reaction mixture was worked up using thin layer chromatography two additional compounds were isolated (the yields are given in parentheses in the scheme below).



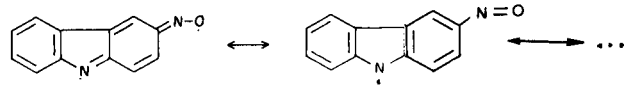
The reaction of I with ethyl iodide proceeds in a quite similar manner although the total yield is lower. 3-Nitroso-9-ethylcarbazole (mp 95-98°) is the main product (11%). 9,9'-Diethyl-3-azoxy- (mp 196-197°) and -3-azocarbazoles (mp 204-205°) were also isolated in 5.1% and 3.8% yield respectively. The fourth product isolated in a minute amount as yellow plates, mp >360° has not yet been identified (monosubstituted 3-azocarbazole?). 3-Nitroso-9-methylcarbazole and its 9-ethyl homologue form greenish-yellow needles melting without decomposition to bright green liquids.

The next experiments are aimed at explaining the formation of the azoxy and azo compounds during alkylation of I. The substrate I is not changed when it is heated in alkaline aqueous acetone for several hours. Addition of potassium iodide to such a solution causes formation of 3-aminocarbazole and a large amount of tar. However the iodide anion cannot act as the reducing agent during the alkylation process because the results of methylation with the aid of dimethyl sulfate were reminiscent of those described above: VI (31%), VII (2.6%) and traces of V were isolated. In all experiments ⅓ of the substrate was converted into crystalline products while the rest formed indefinite tars. The conclusion is that the alkylation of I is accompanied with the red-ox process in which 3-nitroso-9-alkylcarbazoles act as the oxidizing agents and 3-nitrosocarbazolate anion is the reducing agent. The following mechanism of the reaction is proposed.





The first steps resemble closely condensation of nitrosobenzene and *N*-phenylhydroxylamine in an alkaline medium. *N*-Methylation of the hypothetical intermediate VIII causes cleavage of the N-N bond and formation of the nitroso compound V. Until one pyrrole nitrogen remains unsubstituted the intermediates VIII, IX and X can act as the electron acceptors in the red-ox process. The reducing agent is the 3-nitrosocarbazolate anion which forms a free radical.



Dimerization of such radicals and the further oxidation of the dimer containing intact nitroso group provides the mixture of strongly coloured aligomers reported as "tars".

EXPERIMENTAL

3-Nitrosocarbazole.

9-Nitrosocarbazole (39.20 g, 0.2 mole) was dissolved in 600 ml of warm acetic acid and the solution was rapidly cooled to the temperature of 10-12°. To the intensely stirred suspension cncentrated hydrochloric acid (240 ml) was dropped in. A brown viscous solution was stirred for 0.5 hour at room temperature and poured into 1 liter of cold 20% aqueous sodium acetate solution. A green precipitate was collected by filtration, washed with water until neutral and dried. The crude product was suspended in 900 ml of benzene and intensely stirred for 0.5 hours. The insoluble material was collected, dried and crystallized from ethanol boiling with charcoal. 3-Nitrosocarbazole, mp 191-197°, was obtained in 72% yield. Recrystallization gave 22.40 g (57%) of the pure product, mp 197-199° dec; ms: m/e 197 (8.2), 196 (57.4, M⁺), 181 (1.3), 180 (1.8), 167

(14.7), 166 (100.0), 140 (13.1), 139 (39.3); ir (potassium bromide): 750, 780, 830, 915 (out of plane hydrogen wagging in monosubstituted carbazole system), 1100 (Ar-NO stretching vibrations), 1340, 1390 (N-O stretch in *trans* nitroso dimer); 3060, 3090 (C-H stretch), 3160, 3180, 3220 (N-H stretching vibrations).

Anal. Calcd. for $C_{12}H_8N_2O$ (196.20): C, 73.48; H, 4.11. Found: C, 73.59; H, 4.27.

3-Nitrocarbazole.

3-Nitrosocarbazole (1.96 g, 10 mmoles) and 30% hydrogen peroxide (5 ml, 58 mmoles) were dissolved in 100 ml of acetone. Potassium hydroxide (5 ml of 2 *N* aqueous solution) was added and the mixture was left at room temperature for 1 hour. An equal amount of hydrogen peroxide was added and the solution refluxed for 1 hour. The crude product was precipitated with water and crystallized from aqueous 80% ethanol yielding 1.40 g (66%) of 3-nitrocarbazole as reddish-brown rods, mp 214-215°, lit mp 215-216° [11]; ms: m/e 213 (13.8), 212 (100.0, M^+), 196 (2.3), 182 (45.4), 166 (73.1), 165 (11.5), 164 (17.7), 154 (25.4), 139 (64.6); ir (potassium bromide): 730, 760, 820, 855, 905 (nonplanar deformations of aromatic protons and a nitro group), 1320, 1510 (nitro group stretching vibrations), 3070 (C-H stretch), 3345 (pyrrole proton stretching vibrations).

Anal. Calcd. for $C_{12}H_8N_2O_2$ (212.20): C, 67.92; H, 3.77. Found: C, 67.89; H, 3.68.

1-(3-Carbazolyl)-2-naphthol.

To the suspension of 3-nitrosocarbazole (1.96 g, 10 mmoles) in 50 ml of acetic acid sodium nitrite (2.07 g, 30 mmoles) dissolved in 10 ml of water and 0.85 ml of concentrated hydrochloric acid was added. The mixture was stirred at room temperature until the limpid, light brown solution was formed. Potassium hydroxide (5.07 g, 40 mmoles) and 2-naphthol (2.16 g, 15 mmoles) were dissolved in 20 ml of water and the solution was cooled. Both solutions were mixed and the mixture was allowed to stand for 1 hour at room temperature. The crude product was precipitated with water and collected with methylene chloride. The solution was washed with 1 *N* potassium hydroxide and water, dried with anhydrous sodium sulfate and evaporated. The residue was crystallized twice from toluene boiling with charcoal. 1-(3-Carbazolyl)-2-naphthol was obtained (2.30 g, 68%) as brown needles, mp 275-277°, lit mp 277-278° [12]; ms: m/e 338 (25.0), 337 (100.0, M^+), 336 (63.1), 181 (21.0), 166 (36.8), 143 (12.1), 115 (18.4); ir (potassium bromide): 740, 760 (out of plane hydrogen wagging, 4 adjacent protons), 810, 830 (2 adjacent protons), 880 (isolated aromatic proton), 1260 (OH deformations), 3230 (intramolecularly bonded OH), 3415 (pyrrole proton).

Anal. Calcd. for $C_{22}H_{15}N_3O$ (37.37): C, 78.32; H, 4.48. Found: C, 78.50; H, 4.46.

Reaction of I with Nitrous Acid. A.

3-Nitrosocarbazole (1.96 g, 10 mmoles) was suspended in 50 ml of acetic acid and 60 mmoles of sodium nitrite (as a 3 *M* aqueous solution) was added. The mixture was stirred at room temperature for 30 minutes and then at the boiling point for 20 minutes. The solvent was evaporated under reduced pressure. The residue was extracted four times with 150 ml portions of toluene. The extract was concentrated to a small volume and chromatographed on the 5 × 50 cm column (Kieselgel 60, 70-230 mesh), toluene was used as the eluent. The first fraction was concentrated to the volume of 10 ml, an equal volume of *n*-heptane was added and the solution was cooled. 1-Nitrocarbazole (190 mg, 9%) was obtained as yellow rods, mp 189-190°, lit mp 187° [4]; ms: m/e 213 (14.6), 212 (100.0, M^+), 196 (1.3), 182 (4.3), 166 (61.8), 165 (11.0), 154 (3.6), 140 (12.8), 139 (36.0); ir (potassium bromide): 730, 740, 760, 765 (nonplanar deformations of 3 and 4 adjacent aromatic protons), 1340, 1530 (nitro group stretching vibrations), 3060 (C-H stretch), 3400 (pyrrole proton stretching vibrations).

Anal. Calcd. for $C_{12}H_8N_2O_2$: (212.20): C, 67.92; H, 3.77. Found: C, 68.03; H, 3.90.

The second fraction provided 220 mg (10%) of 3-nitrocarbazole, mp and mixed mp 214-216°.

B.

3-Nitrosocarbazole (10 mmoles) was treated with sodium nitrite as before. Urea (3.60 g, 60 mmoles) was added. The mixture was stirred for 10 minutes at room temperature and 10 minutes at the boiling point. The crude, tarry product was precipitated with water, collected by filtration and extracted with boiling toluene. The extract was chromatographed yielding 270 mg (16%) of carbazole, mp and mixed mp 241-243°.

Methylation of 3-Nitrosocarbazole.

Potassium hydroxide (20 ml of 2 *N* aqueous solution) was slowly dropped into a solution of 3-nitrosocarbazole (1.96 g, 10 mmoles) and methyl iodide (1.25 ml, 20 mmoles) in 100 ml of acetone maintained at a temperature of 50°. The mixture was stirred for 2 hours until the deep purple colour ceased and then poured into 500 ml of cold water. The tarry precipitate was collected with chloroform. The solution was dried and evaporated. The residue was dissolved in a minute amount of tetrahydrofuran and chromatographed on 22 plates (20 × 20 cm) covered with a 1 mm layer of Kieselgel G (types 60, E. Merck). Three yellow zones were collected, extracted with boiling acetone and the extracts were evaporated to dryness. The fraction of the highest Rf value (12 mg, 0.7%) was identified as 9,9'-dimethyl-3-azocarbazole, mp 305-306° (DMF); ms: m/e 389 (18.2), 388 (58.0, M^+), 345 (3.0), 208 (1.4), 194 (4.0), 180 (100.0), 165 (2.7), 164 (4.6), 152 (23.9); ir (potassium bromide): 739, 758, 818, 910 (out of plane hydrogen wagging in 3-substituted carbazole system); 1435, 1458 (methyl group deformations), 2830, 2940 (methyl group stretch), 3050 (aromatic protons stretching vibrations).

Anal. Calcd. for $C_{26}H_{20}N_4$ (388.45): C, 80.39; H, 5.19. Found: C, 80.45; H, 5.40.

The main fraction (450 mg, mp 242-248°) was crystallised from a toluene-ethanol mixture providing 9,9'-dimethyl-9-azoxycarbazole, mp 247-248; ms: m/e 405 (4.9), 404 (13.2, M^+), 388 (18.7), 376 (4.2), 210 (6.0), 194 (30.6), 180 (100.0); ir (potassium bromide): 730, 750, 805, 900 (out of plane hydrogen wagging), 1430, 1460 (methyl group deformations), 1470 (asymmetric NNO stretch), 2830, 2935, 3060 (C-H stretching vibrations).

Anal. Calcd. for $C_{26}H_{20}N_4O$ (404.45): C, 77.21; H, 4.98. Found; C, 77.29; H, 5.11.

The third fraction of the lowest Rf value was crystallized from isooctane yielding 181 mg (8.6%) of 3-nitroso-9-methylcarbazole as light green needles, mp 94-95°; ms: m/e 211 (11.0), 210 (75.0, M^+), 180 (100.0), 164 (10.6), 152 (41.0); ir (potassium bromide): 735, 750, 820, 910 (out of plane hydrogen wagging), 1105 (Ar-NO stretching), 1430, 1460 (methyl group deformations), 1512 (N-O stretching vibration), 2930, 3080 (C-H stretch).

Anal. Calcd. for $C_{13}H_{10}N_2O$ (210.23): C, 74.27; H, 4.79. Found: C, 74.41; H, 4.77.

Methylation of I with Methy Sulfate.

Potassium hydroxide (5 ml of 2 *N* aqueous solution) was added to the solution of 1.96 g (10 mmoles) of 3-nitrosocarbazole (I) in 100 ml of acetone. The purple solution was warmed to the boiling point and methyl sulfate (0.94 ml, 10 mmoles) dissolved in 10 ml of acetone was slowly dropped in. When the red colour ceased the next portion of hydroxide (10 mmoles) and methyl sulfate (10 mmoles) were added. The mixture was slowly cooled to room temperature and poured into water. The aqueous solution was discarded, the tarry precipitate was washed with water, collected with tetrahydrofuran and chromatographed. 9,9'-Dimethyl-3-azocarbazole (50 mg) was obtained, mp and mixed mp 305-307° (ethyl acetate). The main fraction provided 600.5 mg of 9,9-dimethyl-3-azoxycarbazole (31%) as before, mp and mixed mp 246-248° (ethyl acetate-DMF). The fraction of the lowest Rf value was extracted with aqueous 80% ethanol. From the cooled solution a minute amount of 3-nitroso-9-methylcarbazole was isolated, mp and mixed mp 90-94°. The insoluble material was dissolved in 5 ml of tetrahydrofuran, the solution filtered diluted with an equal volume of methanol. Brown leaflets (mp >360°) of an unidentified compound were isolated.

Ethylation of I.

The solution of 3-nitrosocarbazole (1.96 g, 10 mmoles) in 100 ml of acetone was treated with ethyl bromide (3.75 ml, 50 mmoles) and warmed to the boiling point. To the intensely stirred solution 2.5 ml of 2 *N* aqueous potassium hydroxide was added. The next portions of the base were added at 0.5 hour intervals, the total amount of potassium hydroxide used was 25 mmoles. The solution was evaporated to dryness under reduced pressure. Chloroform (50 ml) and water (50 ml) were added, the mixture filtered and the layers were separated. The chloroform solution was dried with magnesium sulfate, concentrated and chromatographed on plates as described before. A mixture of benzene and isooctane (9:1) was employed as the developing system. Three fractions were obtained; that of the highest Rf value was crystallized from a benzene-isooctane mixture yielding 80.5 mg (3.8%) of 9,9'-diethyl-3-azocarbazole, mp 200-203°, lit mp 205-206° [10]; ms: m/e 417 (24.0), 416 (77.5, M^+), 388 (2.8), 373 (4.1), 344 (4.5), 210 (13,1), 208 (9.6), 195 (31.9), 194 (100.0), 179 (37.9), 178 (8.3), 167 (5.3); ir (potassium bromide): 735, 750, 825, 895 (out of plane hydrogen wagging); 1385 (symmetric deformations of the methyl group), 1455 (deformations of the methylene group), 2880, 2900 (methylene group), 2940, 2980 (methyl group), 3055 (aromatic protons stretching vibrations).

Anal. Calcd. for $C_{28}H_{24}N_4$ (416.50): C, 80.73; H, 5.81. Found: C, 80.80; H, 5.98.

The intermediate fraction was extracted from the adsorbent with diethyl ether. From the concentrated extract 110.0 mg (5.1%) of 9,9'-diethyl-3-azoxycarbazole was obtained, mp 196-197°, lit mp 194-196° [10]; ms: m/e 433 (11.1), 432 (33.8, M^+), 416 (20.7), 405 (4.9), 404 (15.1), 224 (9.8), 221 (3.6), 211 (14.2), 210 (16.9), 209 (15.6), 208 (48.0), 196 (21.8), 195 (30.7), 194 (100.0), 193 (53.3), 192 (15.1), 182 (9.8), 181 (8.9), 180 (19.1), 179 (57.8); ir (potassium bromide): 730, 750, 820, 900 (out of plane hydrogen wagging), 1390, 1435 (deformations of the ethyl group), 1470 (asymmetric NNO stretch), 2880, 2900, 2940, 2980, 3070 (C-H stretching vibrations).

Anal. Calcd. for $C_{28}H_{24}N_4O$ (432.50): C, 77.75; H, 5.59. Found: C, 77.84; H, 5.70.

The fraction of the lowest Rf value was crystallized from the benzene-*n*-heptane mixture yielding 248.9 mg (11.1%) of 9-ethyl-3-nitrosocarbazole, mp 95-98°.

Anal. Calcd. for $C_{14}H_{12}N_2O$ (224.28): C, 74.97; H, 5.40. Found: C, 75.11; H, 5.51.

The chloroform insoluble material isolated before the chromatographic separation of the aforementioned compounds was dissolved in 10 ml of boiling tetrahydrofuran. Some amorphous strongly coloured products were removed by filtration. The filtrate was diluted with 10 ml of methanol and brown leaflets, mp >360° were collected by filtration. The compound has not been identified.

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