Synthesis and Characterization of New Heterocyclic Derivatives by Oxidation of 1-Amino-2-methylindoline

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1-Amino-2-methylindoline is a precursor used in the synthesis of antihypertension drugs. It reacts with monochloramine to lead to the formation of 1-amino-2-methylindole and azo(2-methyl)indoline. These new products have been isolated and characterized by microanalysis, uv, gc/ms, ir, and $^{1}H/^{13}C$ nmr. The reaction leads to the transient formation of an indolic aminonitrene. 1-Amino-2-methylindole formation proceeds in strongly alkaline medium by rearrangement of a diaziridine intermediate. In neutral or slightly alkaline medium, one obtains a precipitate of tetrazene type (-N-N=N-N-), the azo(2-methyl)indoline. The study of the thermochemical properties shows that tetrazene decomposes towards 150 °C to give the 1,1'-bi(2-methyl)indoline. The stability of the starting reagents and products was the subject of a systematic investigation. A reaction mechanism is proposed.

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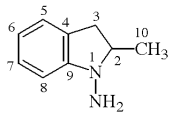
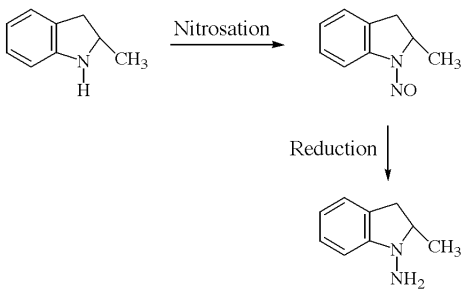
Introduction.

1-Amino-2-methylindoline **2** (NAMI) is used in the pharmaceutical industry as a precursor of antihypertensive drugs whose common international name is *Indapamide*.



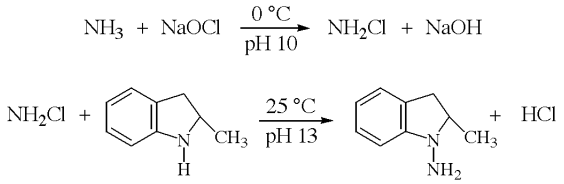
At present, it is prepared by nitrosation of 2-methylindoline **1** (MI) followed by a reduction of nitrosamine with $LiAlH_4$ [1].

Scheme 1



To avoid the nitrosated intermediates, we have undertaken the study of the amination of 2-methylindoline by chloramine in aqueous medium.

Scheme 2



This more environmentally sound route involves numerous secondary products due principally to the oxidizing power of the haloamine upon hydrazine. In addition, the physicochemical analyses show that the aqueous solutions of **1** and **2** undergo a decomposition of these compounds according to time. A preliminary knowledge of their stability is thus necessary. The realization of this process requires a systematic study of the reactions that occur during the synthesis.

This work relates to the stability of **1** and **2** in aqueous solution, the identification of the reaction mechanisms and the characterization of the products formed during the oxidation of 1-amino-2-methylindoline by chloramine. This interaction has not been the object of any former study.

Results and Discussion.

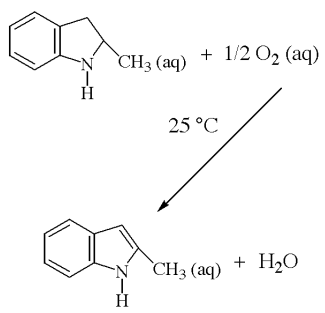
Stability of Indolic Derivatives in Aqueous Medium.

The dissolution of **1** and **2** in water, at different pH, shows an alteration of these compounds, which proceeds visually in a series of colors changes of the solution. No study on the behavior of these products in aqueous medium was published. It is however indicated that the solutions of **2** are stable in concentrated sulphuric acid [2] without bringing more qualitative or quantitative information.

Stability of 2-Methylindoline.

The oxidation of **1** by dissolved oxygen was carried out in aqueous solution saturated by O_2 under atmospheric pressure ([MI] = 10×10^{-3} *M*, [O_2] = 8×10^{-4} *M*). The decomposition is very slow at room temperature. The chromatographic analysis (gc) shows a new product at t_R = 2.13 minutes whose gc/ms analysis attributes this to a molar weight M = 131 g mol^{-1}. The fragmentary study as

Scheme 3



well as a comparison with a reference spectrum [3] prove that it is 2-methylindole **3**, which corresponds to the above reaction.

In alkaline medium ([NaOH] = 0.1 *M*), the MI is more quickly decomposed and that results in successive changes of colors from green to the yellow-brown. Both gc and hplc analyses confirm the disappearance of **1** without appearance of a new peak. The extraction by organic solvents (hexane, ethylether, chlorobenzene) proves that the totality of the products remains in aqueous layer. Acidification of the medium until pH = 6 causes the precipitation of a product which was isolated and analyzed by mass spectrometry. The molecular ion is located at m/z = 264, which corresponds to a dimerized form of **1**. This result is in agreement with the literature, which indicates stable polymer formation starting from indoles and indolines [4-10].

Stability of 1-Amino-2-methylindoline.

Exposed to atmospheric oxygen, the crystals of **2** are unstable and one observes the appearance of a pink-brown color. However, chromatographic analysis shows that the degradation remains superficial and the principal oxidation product is the 1-amino-2-methylindole **4** (table 1) .

Various tests are performed by dissolving **2** (0.015 *M*) in acidic ([HCl] = 0.1 *M*), neutral (pH = 7) and basic ([NaOH] = 0.1 *M*) media. Figure 1 shows a chromatogram obtained for the three zones of pH. Whereas in alkaline medium the principal product is **4**, one obtains in acid medium a mixture of products corresponding to t_R = 1.52, 2.13, 2.37 and 2.88 minutes.

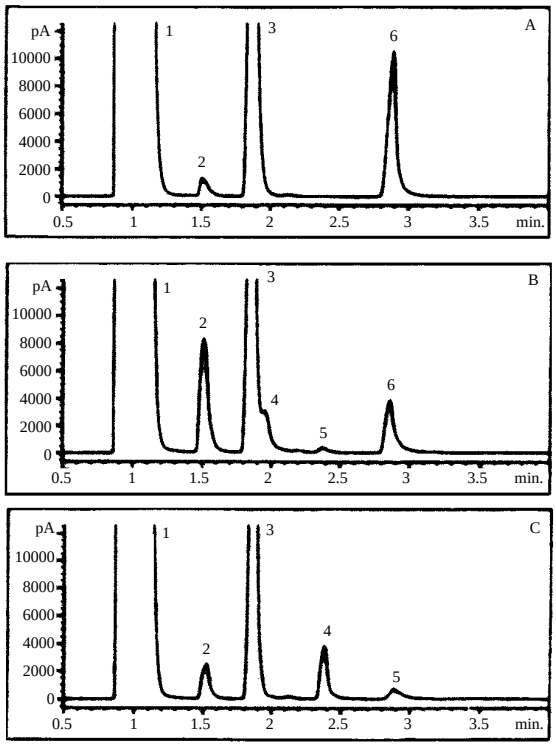


Figure 1. Stability of NAMI in aqueous solution at different pH. **A** pH 13, **B** pH 7, **C** pH 1 (**1** toluene, **2** MI, **3** NAMI, **4** 2-methylindole, **5** 3-methylcinnoline, **6** 1-amino-2-methylindole).

Scheme 4

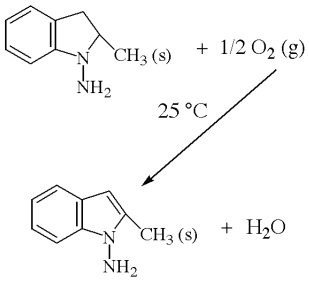


Table 1

Degradation of 1-Amino-2-methylindoline by Atmospheric Oxygen. Analysis of Oxidation Products

Purity (%)	NAMI freshly distilled	NAMI one month later
1-amino-2-methylindoline	99.54	97.9
1-amino-2-methylindole	0.33	1.70
2-methylindole	0.13	0.40

The principal results of gc/ms analyses are consigned in table 2. The peaks of mass m/z = 131, 133 and 146 confirm the presence of **1**, **2** and **3**. The signal located at t_R = 2.37 is characterized by a molecular ion m/z = 144. A study of the reactions of fragmentation in mass spectrometry associated to a comparison with the data libraries converge towards the 3-methylcinnoline **5**. This result is described in the literature, which indicates the existence of an indole-cinnoline rearrangement in acid medium [11,12]. The formation of **5** is described in scheme 5.

In order to avoid any interference, the MI and the NAMI were stored under nitrogen cover, then dissolved in water deprived of oxygen. In particular, the hydrazine crystals are immediately prepared before use and purified by fusion and distillation under vacuum.

Scheme 5

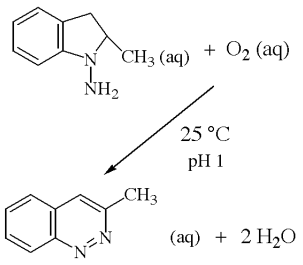


Table 2

Analyses by gc of reaction medium NAMI-O_2 at different pH.

t_R (min)	Molar weight (g mol^{-1})	Compound
1.52	133	2-methylindoline
1.86	148	1-amino-2-methylindoline
2.13	131	2-methylindole
2.37	144	3-methylcinnoline
2.88	146	1-amino-2-methylindole

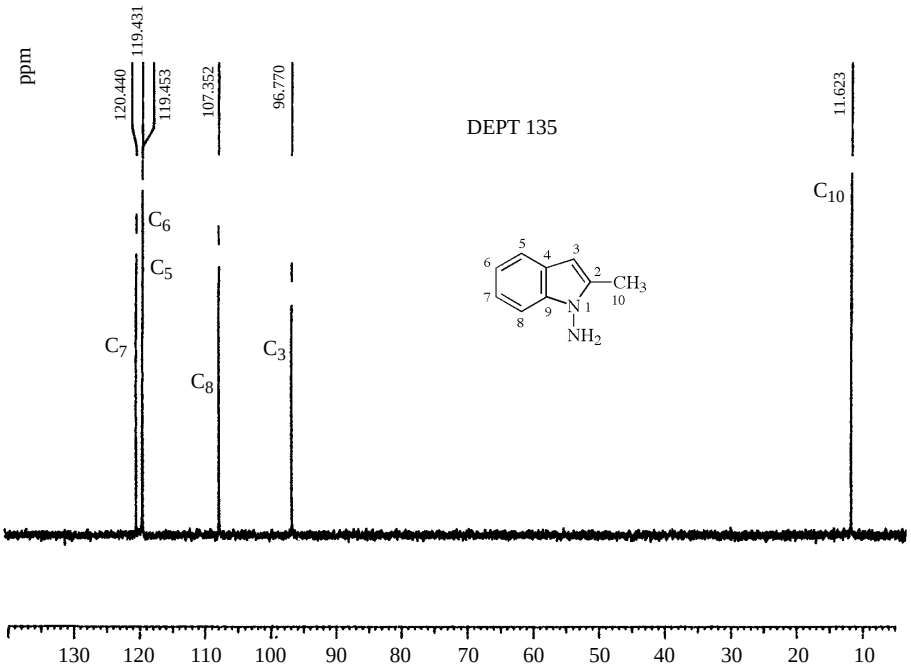


Figure 2. ^{13}C DEPT sequence of 1-amino-2-methylindole.

Oxidation of 1-Amino-2-methylindoline by Chloramine.

Reaction between **1** and NH_2Cl led to the formation of **2** and other products. In particular, the coexistence of an oxidant (chloramine) and a reducer (hydrazine) causes the partial destruction of **2** and the formation of products whose nature depends on the pH.

Synthesis of 1-Amino-2-methylindole.

The reaction carried out at pH = 12.89 and T = 25 °C, under stoichiometric conditions (3 to 10×10^{-3} *M*), shows the formation of a new compound, which exhibits two strong absorption at λ 220 and 280 nm. Analyses by gc indicate the formation of a single product whose instantaneous concentration is proportional to that of the reagents. One observes the decrease of **2** and correlatively the appearance of a signal at 2.88 minutes. Analysis by gc/ms attributes this to a molar weight MW = 146 and an isotopic study of the ions fragments leads to the molecular formula $C_9H_{10}N_2$.

In order to isolate and characterize this product, a complementary experiment was realized in more concentrated medium ([NH_2Cl] = [NAMI] = 0.05 *M*). The brown precipitate formed was filtered, washed, recrystallized in hexane, dried under reduced pressure, and stored under nitrogen atmosphere. Its purity reaches 99.8% (gc). The microanalysis confirms the established formula.

The identification of the product was carried out by comparison with the spectroscopic data of **2**. The ir spectra show in both cases two intense bands at ν 3271 and 3343 cm^{-1} corresponding to vibrations of the NH_2 group. Discrimination between the carbon atoms of pair (CH_2) and odd (CH, CH_3) multiplicities was accomplished by using the standard ^{13}C DEPT sequence [13]. The chemical shifts of the C and H nuclei are given in the experimental section.

Figure 2 presents ^{13}C DEPT sequence of the oxidation product of the NAMI. One remarks a change of parity of C3 carbon (CH type) compared to **2** (CH_2 type). Moreover,

the spectrum shows the disappearance of the C2 signal (quaternary carbon) and the presence of six lines of CH type.

These phenomena prove the appearance of a C2-C3 double bond. Aromatic character of the product is confirmed by the long distance coupling ^3J observed in the ^1H nmr spectrum. The results associated with ir and ms data show that it corresponds to **4**. The stoichiometry of the reaction is unit and the equation is written :

Synthesis of Azo(2-methyl)indoline.

The progressive acidification of the medium induces a decrease in the formation of 1-amino-2-methylindole in favor of a new compound which precipitates and becomes preponderant at pH below 9. At the end of the reaction, the brown solid is filtered, washed, dried under vacuum and characterized by microanalysis, ms, ir, nmr and uv.

The mass spectrum realized by direct introduction (70 eV) exhibits a molecular ion $M^+ = 292$. An isotopic analysis reveals the presence of a peak at m/z = 132 relative to the formation of two half-fragments $C_9H_{10}N$ with release of a nitrogen molecule. The elementary analysis confirms the established formula $C_{18}H_{20}N_4$.

Scheme 6

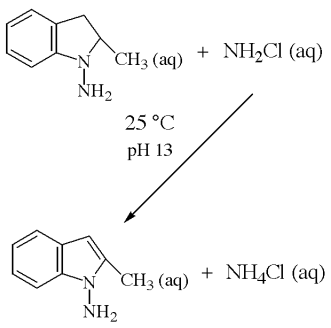


Figure 3 presents the ^{13}C DEPT spectrum. One observes a splitting of the 9 lines, which imply the existence of two identical fragments with a centro-symmetrical formula unit. This fact can be explained by a very close electronic environments linked to the cis-trans isomerism of the azo group. The DEPT sequence (C3 of CH_2 type) and the absence of ν_{NH} band exclude a simple dimerisation of **4**. These results lead to a tetrazene structure (-N-N=N-N-), the azo(2-methyl)-indoline **6**.

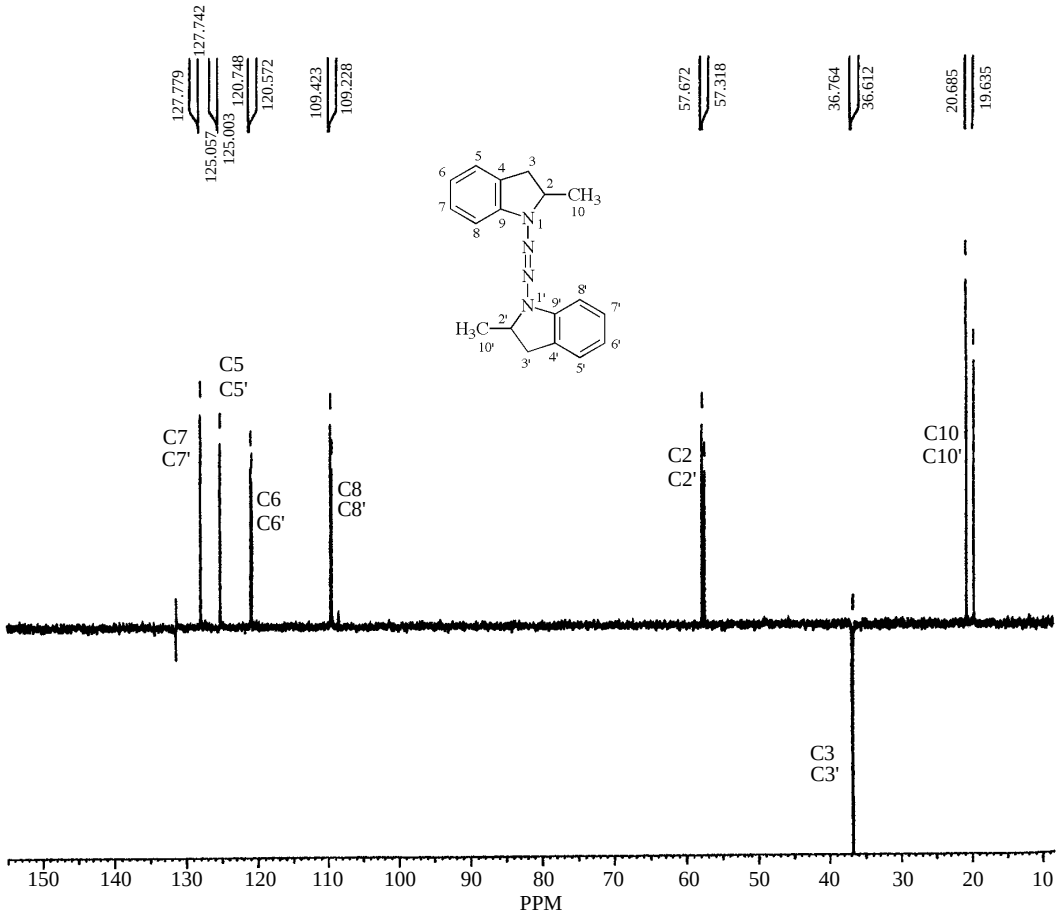


Figure 3. ^{13}C DEPT spectrum of azo(2-methyl)indoline.

Synthesis of 1,1'-Bi(2-methyl)indoline.

The determination of the thermochemical properties of the oxidation products show in the case of **6** a thermal decomposition and the formation of a red-black liquid. The thermal preparation conditions of the last product were studied by coupling differential scanning calorimetry/-thermogravimetric (dsc/tg). Three thermal effects are observed (figure 4).

The first at 80 °C is weakly endothermic (8.37 kJ mol^{-1}) and perfectly reversible between 25 and 100 °C, which corresponds, taking into account the low value of $\Delta_r H$, to a molecular transition. The second begins at 110 °C and is violently exothermic ($\Delta_r H$ = - 236.8 kJ mol^{-1}). The last peak, which corresponds to an endothermic process, is very broad and start at 150 °C ($\Delta_r H$ = 53.2 kJ mol^{-1}). The corresponding mass variations are schematized in the figure 5.

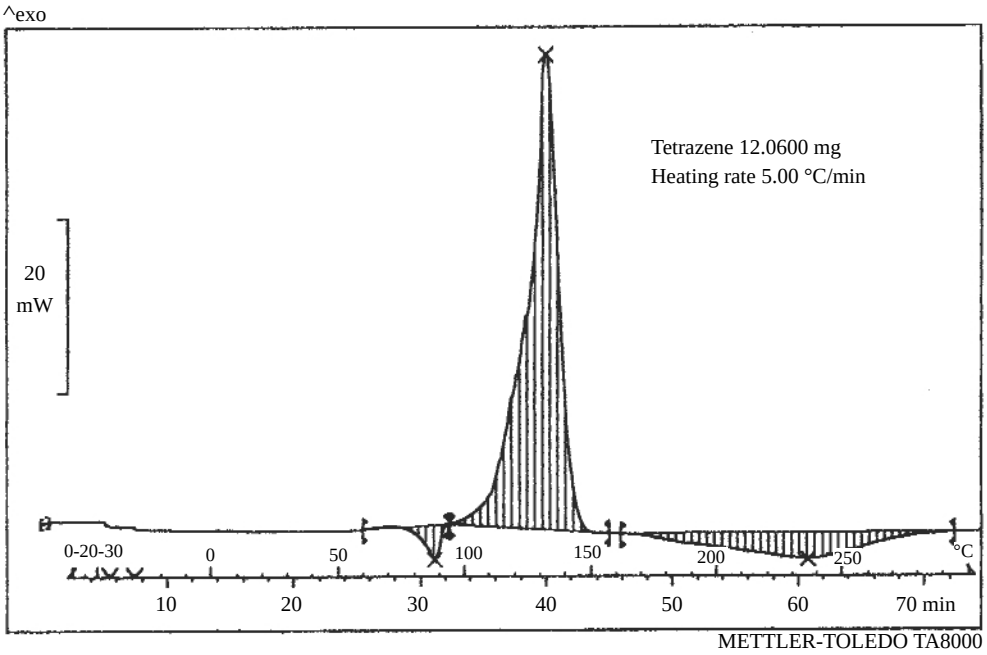


Figure 4. dsc spectrum of azo(2-methyl)indoline.

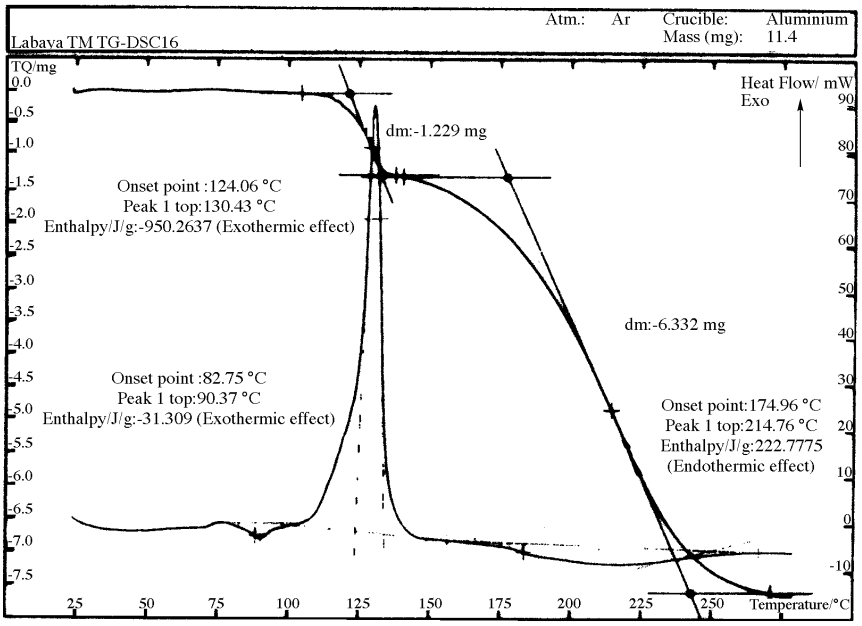
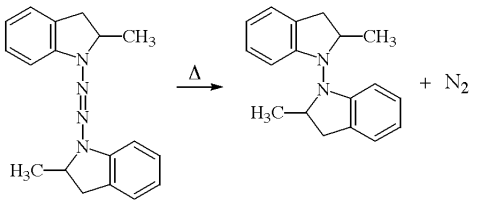


Figure 5. Thermogravimetric analysis of azo(2-methyl)indoline.

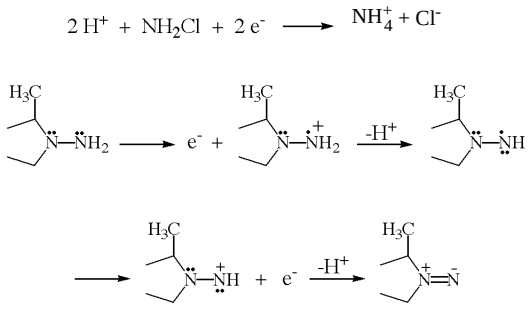
Scheme 7



Starting from 110 °C, the weight loss is carried out in two steps. The first represents a 10% weight loss and corresponds to the exothermic effect. The second extends from 130 °C to 275 °C (Δm/m = 55%) and corresponds to a complete pyrolysis of the initial product **6**. The Δm/m ratio relative to the first signal shows a release of a nitrogen molecule with the formation of an intermediate symmetrical hydrazine, according to the above reaction.

The experimental conditions used by the dsc/tg analysis lead to small amounts of the end product, which are insufficient to a subsequent characterization. Experiments were carried out in thermostatic medium (T = 150 °C) starting from higher quantities of tetrazene. To control the progress of the reaction as a function of time, samples have been analysed by differential scanning calorimetry (dsc). After cooling at 25 °C, a red-black liquid is obtained. Analyses accomplished on the liquid show that the transformation of the tetrazene is incomplete. Indeed, this can result from a solubilization of **6** in the hydrazine formed during the thermal decomposition. The reaction leads to 1,1'-bi(2-methyl)indoline **7** and the microanalysis show the presence of 8% approximately of tetrazene in the final product. The preparative liquid chromatography appears the most suitable to obtain a purity of **7** higher than 92%.

Scheme 8



Reaction Mechanisms

By analogy with the phenomena observed in the oxidation of unsymmetrical dialkylhydrazines [14], the first elementary step corresponds to the formation of a diazene (aminonitrene) [15,16]. The overall two redox half-reactions are described in scheme 8.

Formation of 3-methylcinnoline from 1-amino-2-methylindole under acidic conditions begins with a proton addition on the double bond. Addition of a water is followed by a series of rearrangements which, after aromatization, lead to **5** as shown in scheme 9.

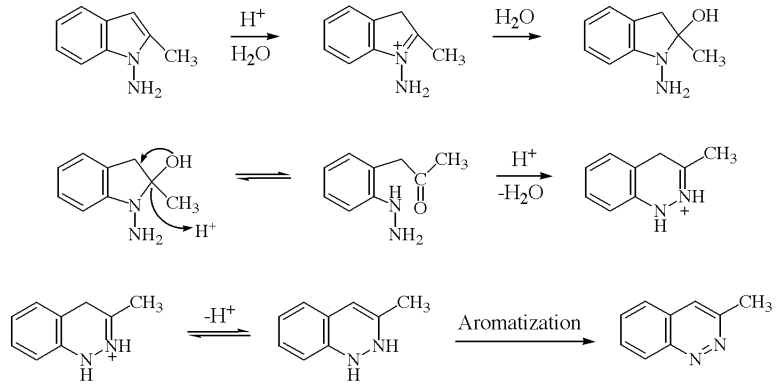
Formation of 1-amino-2-methylindole and azo(2-methyl)indoline from NAMI and chloramine at pH 13 and 9 proceed *via* a nitrene intermediate. The type of product formed is dependent on the pH and the concentration of the nitrene.

At a high pH ([NaOH] = 0.1 *M*), nitrene generation is efficient. Intramolecular C-H insertion proceeds to give the diaziridine intermediate that suffers base-mediated loss of the C3 hydrogen to produce 1-amino-2-methylindole. Aromatization is the driving force behind this event.

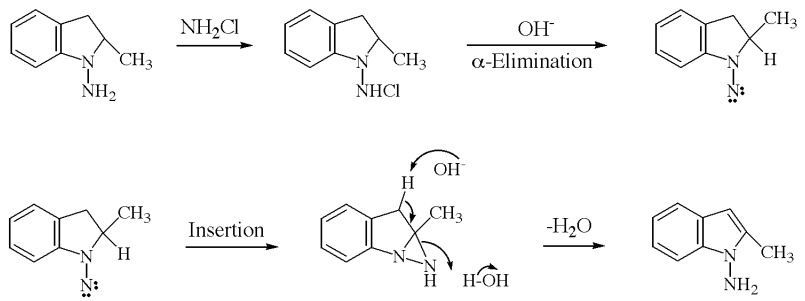
At pH 9, the conversion of the corresponding nitrene is probably slower and incomplete. Unreacted NAMI would be available to trap the nitrene, which would result in a hydrazine derivative. Further oxidation of the hydrazine by chloramine would give the azo(2-methyl)indoline.

This study is in agreement with the major facts observed on the reactivity of the aminonitrenes [16-21]. A mixture of two species **4** and **6** is obtained at intermediate pH values. The present work has allowed us to characterize the products of the reaction between chloramine and

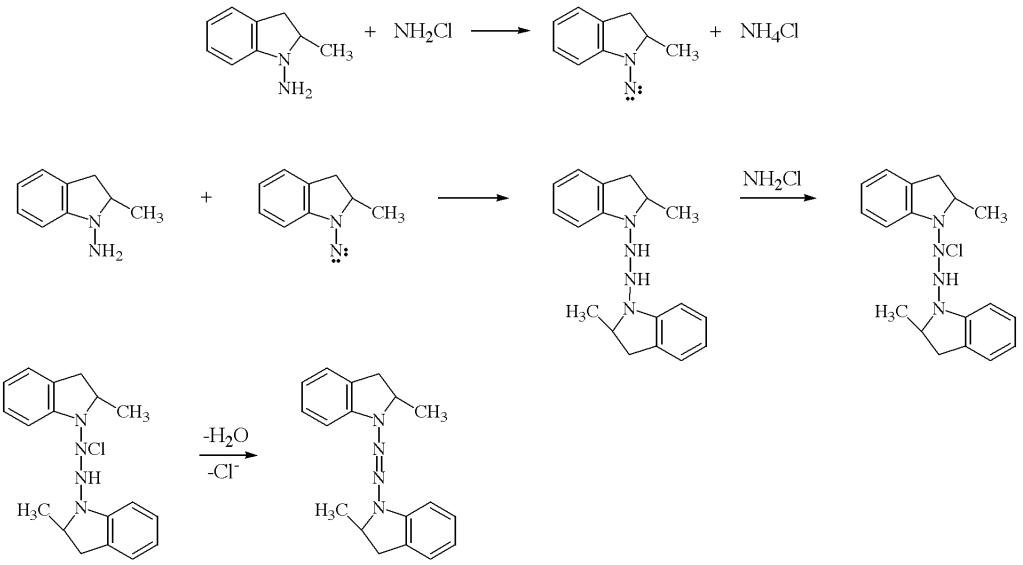
Scheme 9



Scheme 10



Scheme 11



1-amino-2-methylindoline and to demonstrate the fundamental role of pH in the chemistry of the indolic amines and hydrazines.

EXPERIMENTAL

Apparatus.

The nmr spectra were obtained with a high resolution Bruker AM 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C. Samples were recorded in $CDCl_3$ solution with $Si(CH_3)_4$ as the internal standard. The ir and uv spectra were measured with a Beckman 842 instrument (CsI cells) and a Cary IE double beam spectrophotometer, respectively. Analyses by gc were carried out on a HP 6890 chromatograph equipped with EPC modules allowing the control and the measure of the gas flows and the pressures at different levels of the apparatus. The separation was done on a 30 m long HP1 column (100% dimethylpolysiloxane, 530 µm i.d., d_f = 1.5 µm). The gc/ms spectra were acquired with a Delsi Nermag mass spectrometer with a BP 20 capillar column (50 m) and ion source of 70 eV. Thermodynamic data have been determinated using a TA 8000 Mettler system equipped by a DSC 820 modulus acting from -170 to 200 °C under argon sweeping. The trials were carried out by heating (5 °C min^{-1}) using aluminium crucibles and starting from 20 mg of the raw material. The thermogravimetric analyses are performed by means of a Labsys Setaram TG-DSC unit.

Chloramine.

Unstable in water, monochloramine is therefore prepared at -10 °C extemporaneously by reacting 25 mL of sodium hypochlorite 2 *M* and 20 mL of an aqueous NH_3-NH_4Cl solution ($[NH_3]$ = 3.6 *M*, $[NH_4Cl]$ = 2.3 *M*) in the presence of diethylether (40 mL). The organic layer (0.8 to 1 *M* in NH_2Cl) was shaken and washed several times with aliquots of distilled water. Monochloramine in aqueous solution was obtained by re-extraction from the ethereal phase. Its content was determinated by uv spectroscopy at λ 243 nm (ε = 458 M^{-1} cm^{-1}) [22].

1-Amino-2-methylindoline.

This product is not commercially available. It is provided by ORIL INDUSTRIE in the mesylate form after treatment by methane sulphonic acid. Extraction of the hydrazine from the mesylate and its purification was effected according to the following procedure: 60 g of the pink-powder (mesylate) are dissolved in 500 mL of water then neutralized by addition of 60 g of sodium hydroxide. Mixture is then extracted with 120 mL of hexane. Evaporation of the organic solvent yields to a red-brown solid which titrates about 91% with respect to the mesylate. Analysis by gc indicates that the principal impurities are the 2-methylindoline, the 2-methylindole and the 1-amino-2-methylindole. To obtain a high purity product, the crystals are melted and distilled under reduced pressure taking into account the high boiling point of the NAMI (255 °C at 760 Torr). Distillation is carried out under a pressure of 5 Torr. The melting point of the hydrazine is 45 °C. After elimination of the light fractions, the temperature of the boiler reaches 175 °C whereas that of the head of column is established to 130 °C. The temperature of the refrigerant is maintained at 45 °C, which permit to the vapour to condense without crystallisation. NAMI obtained in liquid state is then collected at the room temperature where it crystallizes in the form of white solid. Both gc and elementary analyses show a purity higher than 99%. The principal impurities still present are the MI and the 1-amino-2-methylindole. Because of the instability of the NAMI, the procedure were repeated before each use. This compound being not previously studied, a complete characterization was performed; mp 45 °C, ΔH_f 24.45 kJ mol^{-1}; bp 255 °C, ΔHv 75.48 kJ mol^{-1}; ir: ν NH_2 3303, 3165 cm^{-1}; uv: λ 239 (7150 L mol^{-1} cm^{-1}), 284 (2060 L mol^{-1} cm^{-1}) nm; ms (70 eV): m/z 148 (M^+, 56), 133 (100), 130 (16), 117 (32), 116 (48), 106 (16), 91 (24), 89 (16), 77 (16), 65 (16), 63 (12), 51 (12), 39 (16) 18 (52); ^{1}H nmr ($CDCl_3$): δ 1.43 (3H, d, 6.13, *H_{10}*), 2.5 (1H, q, 11.02, *H_3*), 3.1 (1H, q, 7.73, *H_3*), 3.3 (1H, m, *H_2*), 6.65-6.75 (2H, m, *H_6-H_8*), 7-7.05 (2H, m, *H_5-H_7*); ^{13}C nmr ($CDCl_3$): δ 17.9 (*C_{10}*), 33.8 (*C_3*), 66.77 (*C_2*), 109.2 (*C_8*), 118.5 (*C_6*), 123.5 (*C_5*), 126.8 (*C_7*), 127.1 (*C_4*), 155.1 (*C_9*).

Anal. Calc. for $C_9H_{12}N_2$ (148): C, 72.94; H, 8.16; N, 18.90. Found: C, 72.74; H, 8.15; N, 18.90.

1-Amino-2-methylindole.

By dissolving oxygen in a solution of 1-amino-2-methylindoline at 15×10^{-3} *M*, one observes in basic medium (pH 13) the precipitation of fine needles of 1-amino-2-methylindole. The crystals obtained were filtered, washed, recrystallized in hexane and dried under vacuum. Analysis by gc provides a titre close to 99.8% and the principal impurity is the NAMI; mp 111.4 °C, ΔHf 25.55 kJ mol^{-1}; bp 300.5 °C, ΔH_v 79.55 kJ mol^{-1}; ir: ν NH2 3343, 3271 cm^{-1}; uv: λ 220 (33909 L mol^{-1} cm^{-1}), 280 (6871 L mol^{-1} cm^{-1}) nm; ms (70 eV): m/z 146 (M^+, 100), 145 (26.4), 131 (47), 130 (37), 129 (22.4), 128 (15.2), 118 (34.2), 117 (12.5), 105 (37.6), 104 (79.2), 103 (18.8), 102 (15.3), 91 (15.7), 89 (12.1), 78 (17.9), 77 (29.3), 71 (9.1), 65 (10.9), 63 (16.4); ^{1}H nmr (CDCl3): δ 2.41 (3H, s, *H_{10}*), 6.21 (1H, s, *H_3*), 7.18 (1H, d, 7.56, *H_8*), 7.22 (1H, m, *H_6*), 7.22 (1H, m, *H_7*), 7.60 (1H, d, 7.33, *H_5*); $_{13}$C nmr ($CDCl_3$): δ 11.6 (*C_{10}*), 96.7 (*C_3*), 107.8 (*C_8*), 119.4 (*C_6*), 119.4 (*C7*), 120.4 (*C_5*), 125.6 (*C_4*), 136.9 (*C_2*), 137.8 (*C_9*).

Anal. Calc. for $C_9H_{10}N_2$ (146): C, 73.94; H, 6.89; N, 19.16. Found: C, 73.90; H, 6.90; N, 19.20.

Azo(2-methyl)indoline.

It was synthesized at 5 °C and pH 9 by reacting 1-amino-2-methylindoline and chloramine in stoichiometric conditions (10×10^{-3} *M*). The solid obtained was filtered, washed, recrystallized in hexane and dried under vacuum. Its purity is close to 99.2%; ms (70 eV): m/z 292 (M^+, 6.4), 264 (22.7), 262 (42.7), 261 (17.3), 249 (22.7), 247 (47.3), 232 (10.8), 160 (18.6), 146 (50.2), 143 (15.2), 133 (38.4), 132 (48.9), 131 (66.9), 130 (50.8), 118 (100), 117 (45.8), 104 (14.3), 103 (14.7), 102 (12.9), 91 (44.7), 90 (19.4), 89 (17.7), 77 (23.4), 65 (18.2), 63 (13.4); ^{1}H nmr ($CDCl_3$): δ 1.50 (3H, d, 1.86, *H_{10}/$H_{10'}$*), 1.52 (3H, d, 1.88, *H_{10}/$H_{10'}$*), 2.77-2.88 (2H, q, 5.75, *H_3/$H_{3'}$*), 3.42-3.54 (2H, m, *H_3/$H_{3'}$*), 4.65-4.72 (2H, m, *H_2/$H_{2'}$*), 6.85-6.96 (2H, m, *H_6/$H_{6'}$*), 7.14-7.26 (2H, m, *H_5/$H_{5'}$*), 7.14-7.26 (2H, m, *H_7/$H_{7'}$*), 7.14-7.26 (2H, m, *H_8/$H_{8'}$*); ^{13}C nmr ($CDCl_3$): δ 19.64/20.69 (*C_{10}/$C_{10'}$*), 36.61/36.76 (*C_3/$C_{3'}$*), 57.30/57.67 (*C_2/$C_{2'}$*), 109.23/109.42 (*C_8/$C_{8'}$*), 120.57/120.75 (C_6/$C_{6'}$), 125.00/125.05 (*C_5/$C_{5'}$*), 127.10 (*C_4/$C_{4'}$*), 127.74/127.78 (*C_7/$C_{7'}$*), 146.7 (*C_9/$C_{9'}$*).

Anal. Calc. for $C_{18}H_{20}N_4$ (292): C, 73.94; H, 6.89; N, 19.16. Found: C, 73.87; H, 6.92; N, 19.21.

1,1'-Bi(2-methyl)indoline.

It is obtained by pyrolysis of the tetrazene at 150 °C during several hours. One forms a red-black liquid of which the purity does not exceed 95%. The principal impurity is the azo(2-methyl)indoline.

Anal. Calc. for 92% $C_{18}H_{20}N_2$ (264) + 8% $C_{18}H_{20}N_4$ (292): C, 81.15; H, 7.52; N, 11.33. Found: C, 81.15; H, 7.57; N, 11.28.

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