Oxidation and Acid-Catalyzed Cyclization of Aldehyde 2-Aminophenylhydrazones. Alternative Syntheses for 1,2,4-Benzotriazines and Benzimidazoles

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Aldehyde 2-aminophenylhydrazones are easily oxidized by air to 3-substituted 1,2,4-benzotriazines. In two cases the intermediate 3,4-dihydro-1,2,4-benzotriazines were isolated. In the absence of oxygen, acids catalyze the formation of 2-substituted benzimidazoles with loss of ammonia. It is suggested that both reactions proceed *via* 1,2,3,4-tetrahydro-1,2,4-benzotriazines (III), formed by addition of the amino group on the hydrazone double bond. Such cyclic forms (III) predominate over the open chain structures (II) in the cases of aliphatic and arylalkyl-aldehyde 2-aminophenylhydrazones, as supported by nmr spectra, while benzaldehyde 2-aminophenylhydrazone exists mainly or exclusively in the open chain form (II).

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In the foregoing publication (1), the structure IV (R′-R′′ = $(CH_2)_5$) of cyclohexane-3-spiro-3,4-dihydro-1,2,4-benzotriazine was assigned to the product obtained by sodium dithionite reduction of cyclohexanone 2-nitrophenylhydrazone (2,3). Moreover, it was shown that this compound could be prepared more easily through the air oxidation of the 2-aminophenylhydrazone resulting from catalytic hydrogenation of the nitro derivative.

In the same way, starting from 2-nitrophenylhydrazones of unhindered or slightly hindered ketones, a number of 3,3-disubstituted 3,4-dihydro-1,2,4-benzotriazines were also prepared (4). A great amount of steric hindrance on the hydrazone double bond prevented the formation of 3,4-dihydro-1,2,4-benzotriazines.

Extension of the above sequence of reactions to aldehyde 2-nitrophenylhydrazones, whose hydrazone double bond is clearly less hindered, should be expected to readily give the corresponding 3-monosubstituted 3,4-dihydro-1,2,4-benzotriazines (IV, R′′ = H) or the 3-substituted 1,2,4-benzotriazines, by further oxidation of the former.

However, it is known (5,6,7,8) that reduction with tin or stannous chloride and hydrochloric acid of some aldehyde 2-nitrophenylhydrazones gives rise to benzimidazole derivatives. Therefore, we decided to examine separately the action of oxygen and of acid on aldehyde 2-aminophenylhydrazones obtained as pure as possible through catalytic reduction of the corresponding nitro derivatives.

The exact correspondence between observed and calculated volumes of hydrogen absorbed during the reduction does not leave any doubt as to the purity of the 2-aminophenylhydrazones of formic, acetic, propionic and phenylacetic aldehydes so obtained which were then used without further purification in order to avoid any unnecessary exposure to air. Catalytic hydrogenation of benzaldehyde 2-nitrophenylhydrazone did not stop spontaneously when the calculated volume of hydrogen was absorbed, indicating the presence of other competitive reductions. In this case a chromatographic purifiction of the amino compound was unavoidable. However, once pure, benzaldehyde 2-aminophenylhydrazone was more stable than the remaining 2-aminophenylhydrazones.

According to the observations of several Authors (9) concerning aldehyde phenylhydrazones, the nmr spectra of aldehyde 2-aminophenylhydrazones should show peaks for the methine protons (II; R′′ = H) in the aromatic region ($6.1 \leq \delta \leq 7.7$). While this is true for benzaldehyde 2-aminophenylhydrazone, all the remaining aldehyde 2-aminophenylhydrazones show no additional hydrogen atoms or only small fractions of one proton in this region. Rather, these compounds show peaks at much higher fields ($3 \leq \delta \leq 4.5$), suggesting, according to Shoolery rules (10), the presence of a hydrogen atom like that on position 3 of 1,2,3,4-tetrahydro-1,2,4-benzotriazines (III; R′′ = H).

Thus, nmr spectra further support the claimed (1) equilibrium between 2-aminophenylhydrazones (II) and tetrahydrobenzotriazines (III). Calculations performed on the integrated values of the methine proton peaks compared with those of the aromatic hydrogen atoms and with thoseof hydrogen atoms removed by deuterium dioxide exchange, allowed us to conclude that the cyclic structure III is definitively more prevalent (81-100%) than structure II for aliphatic or arylaliphatic aldehyde derivatives, while structure III occurs only to the extent of, at the most, 5% of the benzaldehyde derivative.

Accordingly, the air oxidation of all aldehyde 2-aminophenylhydrazones gives rise to the corresponding 1,2,4-benzotriazines, but yields are good only for aliphatic or arylaliphatic aldehyde derivatives. Formation of the

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benzotriazines follows that of the 3,4-dihydro derivatives, which in two instances (IV; R'' = H, R' = CH_3 and C_2H_5) were isolated and characterized.

Formation of 3,4-dihydro 1,2,4-benzotriazines is, however, always evident through the intense purple colour, given with acids, exhibited by the reaction mixtures. Since several tautomeric structures are possible for the dihydrobenzotriazines, we point out that their uv spectra are identical with those of 3,4-dihydrobenzotriazines which are disubstituted at position 3 (1,4), suggesting a similar structure. Moreover nmr spectra indicate the exchange of only one hydrogen atom by deuterium oxide and also spin-spin coupling between the proton on position 3 and those on the aliphatic chains located at the same ring position. Thus, 1,2- or 1,4-dihydrobenzotriazine structures were excluded, since they would involve the loss of two protons by deuterium oxide exchange and a reduced multiplicity for the signals due to the aliphatic chains at position 3.

The isolated 3,4-dihydrobenzotriazines are readily converted to the corresponding benzotriazines by further exposure to the air. Therefore, air oxidation of aldehyde 2-aminophenylhydrazones represents an alternative method for the synthesis of benzotriazines, which is competitive with well established methods of preparation (11-16).

It is worth noting that in the case of benzaldehyde 2-aminophenylhydrazone oxidation together with 3-phenyl 1,2,4-benzotriazine, we isolated a new compound identified as 1-benzoylamino-2-phenylbenzimidazole (VI), whose formation is somewhat intriguing. It is known that aromatic aldehyde phenylhydrazones take up oxygen easily to form azohydroperoxides which decompose thus forming *via* different pathways, benzene, aromatic acids and aldehydes, aroylphenylhydrazines and aroylazobenzenes (17,18). The benzaldehyde actually formed during the oxidation of benzaldehyde 2-aminophenylhydrazone could provide the C_6H_5-C portion required for closure of the benzimidazole ring of VI.

Dibenzylidene-2-aminophenylhydrazine is not an intermediate in the formation of VI, since it is recovered practically unchanged even after exposure to oxygen for extended periods of time. On the other hand, a small amount of compound VI was obtained by bubbling air through a solution of benzaldehyde and *N*-(2-amino)phenyl-*N'*-benzoylhydrazine. The mechanism for the formation of compound VI certainly deserves further investigation.

The action of acid on aldehyde 2-aminophenylhydrazones was then investigated by treating these compounds with 2.5*N* ethanolic hydrochloric acid at room temperature and avoiding the above mentioned oxidative reactions by rigorous air exclusion. As expected, 2-substituted benzimidazoles were formed with simultaneous loss of ammonia. Aliphatic and aromatic aldehyde derivatives behaved similarly and in all cases benzimidazoles were isolated in good yields (67-86%).

Thus, the acid-catalyzed cyclization of aldehyde 2-aminophenylhydrazones is a good alternative route to benzimidazoles, thus supplementing conventional methods (19). Although this method is somewhat more elaborate than most of the conventional ones, it shoud be particularly suitable for the synthesis of benzimidazoles containing sensitive groups in the 2 position.

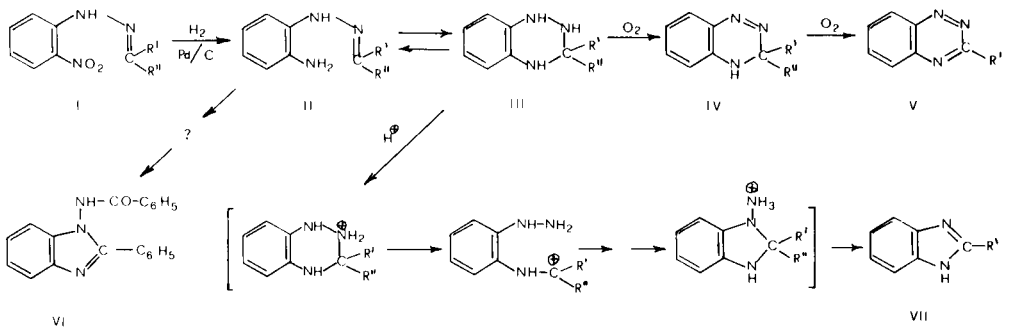
A reasonable explanation of benzimidazole ring formation requires the migration of an alkylidene or an arylidene group from the hydrazine moiety to the amine nitrogen atom, through the protonated 1,2,3,4-tetrahydro-1,2,4-benzotriazines (III). A somewhat similar acyl-group migration was described by Abramovitch and Schofield (13) and later by Boido and Sparatore (20).

In conclusion, the tetrahydrobenzotriazines III act as common intermediates for both benzotriazine and benzimidazole formation. The nature of the heterocycles thus obtained is strictly dependent on availability of oxygen and the acidity of the experimental conditions.

EXPERIMENTAL

Melting points are uncorrected. The uv and ir spectra were recorded, respectively, on a Hitachi Perkin-Elmer model EPS 3T, and on a Unicam SP 200 spectrophotometer. Nmr were determined on a Hitachi Perkin-Elmer model R 24 spectrometer, using deuterochloroform as the solvent and TMS as the internal standard. Mass spectra were obtained with a Varian mass spectrometer GS/MS system MAT/III. Elemental analyses were perfomed at the Microanalytical Laboratory of the Istituto di Chimica farmaceutica e tossicologica of Genoa University.

Aliphatic Aldehyde 2-Aminophenylhydrazones (II) [1,2,3,4-Tetrahydro-1,2,4-benzotriazines (III)].



Aldehyde 2-nitrophenylhydrazones (Ia-Id) dissolved in peroxide free tetrahydrofuran (20 ml. for each 1 g.) were hydrogenated at room temperature and at atmospheric pressure in the presence of 10% palladium on charcoal (50 mg. for each 1 g.) until hydrogen absorption stopped spontaneously. The absorbed volumes of hydrogen differed from theoretical calculated values by less than 2%.

The hydrogenations were carried out in a flask designed to allow catalyst filtration without exposing the solution to the air. After filtration of the catalyst, the solvent was removed under reduced pressure leaving colourless or off-white crystalline residues; the formaldehyde derivative was obtained as an oil. All products were prepared just prior to use and were stored to avoid contact with air as much as possible.

Compound IIa/IIIa (R′ = R′′ = H).

This compound was obtained as an oil from Ia; nmr (under nitrogen): δ 7.03-6.30 (m, 4.38H, aromatic H + CH_2=N-), 4.08 (s, 1.62H, CH_2 <), 3.78 (large s, 3H, disappears after deuterium oxide exchange, 3 NH).

Anal. Calcd. for $C_7H_9N_3$: C, 62.20; H, 6.71; N, 31.09. Found: C, 62.06; H, 6.52.

The results for several nitrogen determinations were always lower than that expected by more than 1%.

Compound IIb/IIIb (R′ = CH_3; R′′ = H).

This compound had m.p. 90-92°; nmr: δ 7.30-6.30 (m, 4.08H, aromatic H + R′-CH=N), 4.50-3.72 (m, 3.92H, 0.92H after deuterium oxide exchange, 3 NH + R′-CH <), 1.80 (d, 0.25H, *CH_3*-CH=N), 1.18 (d, 2.75H, *CH_3*-CH <).

Anal. Calcd. for $C_8H_{11}N_3$: C, 64.40; H, 7.43; N, 28.16. Found: C, 64.20; H, 7.55; N, 27.89.

Compound IIc/IIIc (R′ = C_2H_5; R′′ = H).

This compound had m.p. 66-69°; nmr: δ 7.10-6.30 (m, 4 aromatic H), 4.30-3.50 (m + t, 4H, 1H after deuterium oxide exchange, 3 NH + R′CH <), 1.85-0.70 (m, 5H, C_2H_5).

Anal. Calcd. for $C_9H_{13}N_3$: C, 66.23; H, 8.03; N, 25.75. Found: C, 66.04; H, 7.76; N, 25.21.

Compound IId/IIId (R′ = $CH_2C_6H_5$; R′′ = H).

This compound had m.p. 100-101°; nmr: δ 7.35-6.35 (2 m, 9 aromatic H), 4.35-3.80 (m, 4H, 1H after deuterium oxide exchange, 3 NH + R′-CH <), 3.30-2.50 (m, 2H, CH_2).

Anal. Calcd. for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.23; H, 6.82; N, 18.46.

Benzaldehyde 2-Aminophenylhydrazone (IIe).

Benzaldehyde 2-nitrophenylhydrazone (2 g.) was reduced as above in the presence of 5% palladium on charcoal (200 mg.). Hydrogen absorption did not stop after the calculated volume for nitro group reduction was already taken up, thus indicating that other competitive reductions were occurring. At this point the hydrogenation was interrupted, the catalyst filtered and the solution concentrated to a small volume under reduced pressure. The residue was then chromatographed on 50 g. of neutral alumina (activity I Brockmann scale) eluting with dichloromethane.

Firstly, 0.18 g. of unchanged 2-nitrophenylhydrazone were recovered, followed by 1.30 g. (yield 77%) of yellow needles, which, after recrystallization from ethanol, melted at 138-139°; Franzen (5) reported m.p. 142°. In its pure form this compound is fairly stable; uv (ethanol): λ max nm (log ε) 242.5 sh (4.14), 298 (3.87), 352.5 (4.24); nmr: δ 7.80-6.60 (m, 10H, 9 aromatic H + R′-CH=N), 3.40 (very large s, 3H, 3 NH); ms: m/e (relative intensity, %) 212 (6), 211 (35) M^+, 134 (12) M^+-C_6H_5, 107 (100) M^+ -C_6H_5CHN.

Air Oxidation of 2-Aminophenylhydrazones.

Aldehyde 2-aminophenylhydrazones were dissolved in ethanol (20 ml. for each 1 g.), or in a mixture of ethanol-tetrahydrofuran (4/1, v/v) when R′ = C_6H_5, and air was bubbled through the solution for 6-10 hours (36 hours when R′ = C_6H_5), following the course of oxidation by uv spectra and tlc (silicon dioxide dry ether-hexane, 1/1 v/v). The solvent was removed under reduced pressure and the residue was chromatographed on alumina or silica gel (R′ = CH_3 and C_6H_5), using as eluent dry ether (R′ = H), dichloromethane (R′ = C_6H_5), or a 1:1 (v/v) mixture of dry ether and hexane (R′ = CH_3) or dichloromethane and hexane (R′ = C_2H_5 and CH_2-C_6H_5).

3-R′-Benzotriazines (V) were always obtained as the first fractions (yield for R′ = H: 41%; CH_3: 32%; C_2H_5: 7.5%; $CH_2C_6H_5$: 58%; C_6H_5: 14%). Eluting the column further, 3,4-dihydro-1,2,4-benzotriazines (IV) were recovered (62% yield for R′ = CH_3; 67% for R′ = C_2H_5) or, when R′ = C_6H_5, 1-benzoylamino-2-phenylbenzimidazole (VI) was obtained in 27% yield (calculated on the basis of one mole for two moles of 2-aminophenylhydrazone).

3-R′-1,2,4-Benzotriazines (V).

Compound Va (R′ = H).

This compound was obtained as yellow needles, m.p. 71-72° [lit. (13) m.p. 76-77°]; uv (ethanol): λ max nm (log ε) 231.5 (4.78), 304.5 (3.57), 321 sh (3.45), 4.34 (2.46); ms: m/e (relative intensity, %) 132 (6), 131 (52) M^+, 104 (11), 103 (94) M^+-2N, 77 (15), 76 (100) $C_6H_4^+$, 75 (15), 74 (19).

Compound Vb (R′ = CH_3).

This compound was obtained as yellow needles, m.. 97-98° [lit. (13) m.p. 97-98°]; uv (ethanol): λ max nm (log ε) 233.5 (4.40), 303 (3.59), 330 sh (3.44), 438 (2.48); ms: m/e (relative intensity, %), 146 (3), 145 (14) M^+, 118 (9), 117 (100) M^+-2N, 116 (9), 91 (7), 90 (10), 89 (6), 77 (70), 76 (81) $C_6H_4^+$, 75 (16), 74 (16).

Compound Vc (R′ = C_2H_5).

This compound was obtained as a yellow oil; uv (ethanol): λ max nm 235, 297, 330, 440; nmr: δ 8.4-7.4 (m, 4 aromatic H), 3.43 (q, 2H, CH_2), 1.55 (t, 3H, CH_3).

Anal. Calcd. for $C_9H_9N_3$: C, 67.90; H, 5.70; N, 26.40. Found: C, 68.01; H, 5.85; N, 25.99.

Compound Vd (R′ = $CH_2C_6H_5$).

This compound was obtained as yellow needles, m.p. 85-86° [lit (21) m.p. 87°]; uv (ethanol): λ max nm (log ε) 235 (4.42), 305 (3.67), 327 sh (3.51), 440 (2.51); nmr: δ 8.60-6.90 (m, 9 aromatic H), 4.69 (s, 2H, CH_2).

Compound Ve (R′ = C_6H_5).

This compound was obtained as yellow crystals, m.p. 123-125° [lit (13) m.p. 126-127°]; uv (ethanol): λ max nm (log ε) 258.5 (4.26), 272 sh (4.11), 325 (3.94), 440 (2.53); ms: m/e (relative intensity, %) 208 (4), 207 (100) M^+, 206 (21), 180 (5), 179 (9) M^+-2N, 178 (7), 105 (7), 103 (11), 77 (15), 76 (42), $C_6H_4^+$, 75 (9).

3-R′-3,4-Dihydro-1,2,4-benzotriazines (IV).

Compound IVb (R′ = CH_3; R′′ = H).

This compound was obtained as yellow crystals, m.p. 91-92°; uv (ethanol): λ max nm 226, 246 sh, 287, 353, 445; λ max (1*N* hydrochloric acid): nm 234, 300 sh, 345, 510; nmr: δ 7.90-6.50 (m, 4 aromatic H), 4.40-3.60 (s + q, 2H, NH-CH <), 1.80 (d, 3H, CH_3), after deuterium oxide exchange a quadruplet centered at δ 4.1 (-CH<) remains; ms: m/e (relative intensity, %) 147 (9) M^+, 119 (100) M^+-2N, 118 (53) $(C_6H_4NCHCH_3)^+$, 104 (65) $(C_6H_4N_2)^+$, 91 (35) $(C_6H_5N)^+$.

Anal. Calcd. for $C_8H_9N_3$: C, 65.29; H, 6.16; N, 28.55. Found: C, 65.36; H, 6.12; N, 28.56.

Compound IVc (R′ = C_2H_5; R′′ = H).

This compound was obtained as yellow crystals melting at 60-62°; uv (ethanol): λ max nm 227, 247 sh, 286, 352, 443, λ max (1*N* hydrochloric acid): nm 234, 300 sh, 345, 510; mmr: δ 7.82-6.45 (m, 4 aromatic H), 4.50-3.80 (s + t, 2H, NH-CH <), 2.45-1.90 (m, 2H, CH_2), 1.18 (t, 3H, CH_3), after deuterium oxide exchange a triplet at δ 3.98 (-CH <) remains; ms: m/e (relative intensity, %) 101 (4) M^+, 133 (100) M^+-2N, 118 (31), 104 (56) $[C_6H_4N_2]^+$.

Anal. Calcd. for $C_9H_{11}N_3$: C, 67.05; H, 6.88; N, 26.07. Found: C, 67.22; H, 6.71; N, 25.98.

1-Benzoylamino-2-phenylbenzimidazole (VI).

The crude product obtained from the chromatography was crystallized from ethanol-ether giving white needles melting at 184-185°; uv (ethanol): λ max nm (log ε) 230 sh (4.40), 278.5 (4.18), 290.5 (4.23); ir (5% in potassium bromide): 1685 (*CO*-NH), 3060 cm^{-1} (NH); nmr (acetone-d_6): δ 7.80-6.80 (m, 14 aromatic H), in offset a singlet appears at δ 11.50 (*NH*-CO) which disappears slowly by deuterium oxide exchange; ms: m/e (relative intensity, %) 314 (5), 313 (20) M^+, 208 (5) M^+-C_6H_5CO, 194 (21) M^+-C_6H_5CON, 194 (12), 119 (31) $(C_6H_5CON)^+$, 105 (100) $(C_6H_5CO)^+$.

Anal. Calcd. for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.83; N, 13.41. Found: C, 76.42; H, 4.91; N, 13.13.

Oxidation of 3,4-Dihydro-1,2,4-benzotriazines.

Air was bubbled through an ethanolic solution of 3,4-dihydro-1,2,4-benzotriazines until the typical purple colour test given with hydrochloric acid was negative. Oxidation also takes place in acidic solution, thus air could be bubbled through a solution of dihydrobenzotriazines in ~ 2.5*N* ethanolic hydrochloric acid until the purple colour was replaced by the light yellow colour of benzotriazines. The solution was made basic and ethanol removed under reduced pressure; the residue was extracted with ether and the ether solution was chromatographed on silica gel. Thus, 3-methyl and 3-ethyl-1,2,4-benzotriazine were obtained in 77% and 81% yield, respectively.

Dibenzyliden-2-aminophenylhydrazine.

An ethanolic solution (50 ml.) of benzaldehyde 2-aminophenylhydrazone (0.93 g.) and benzaldehyde (0.47 g.) was refluxed under nitrogen for 1 hour. The solvent was removed under reduced pressure and the residue chromatographed on silica gel (30 g.) eluting with dichloromethane. Firstly, 1.08 g. (82% yield) of the title compound were obtained, followed by 0.14 g. of oil and then by 60 mg. of 2-phenylbenzimidazole (m.p. and mixed m.p. 280-283°). Dibenzyliden-2-aminophenylhydrazine was crystallized from ether obtaining yellow needles with m.p. 107.5-109.5°; uv (ethanol): λ max nm (log ε) 265 sh (4.01), 297.5 (3.99), 364 (4.25); ms: m/e (relative intensity, %) 300 (4), 299 (14) M^+, 298 (5), 297 (20), 296 (13), 195 (55) M^+-C_6H_5CHN, 194 (100) M^+-C_7H_7N, 149 (28), 105 (22) $(C_7H_7N)^+$, 104 (20) $(C_6H_5CHN)^+$.

Anal. Calcd. for $C_{20}H_{17}N_3$: C, 80.24; H, 5.72; N, 14.04. Found: C, 80.33; H, 5.80; N, 13.73.

Oxidation of Dibenzyliden-2-aminophenylhydrazine.

Air was bubbled for 36 hours through an ethanolic solution of the above compound (1 g. in 40 ml.). The solvent was removed and ether was added to the residue, recovering 0.83 g. of starting material. No defined products could be obtained from the ether soluble material.

N-(2-Benzylidenamino)phenyl-*N'*-benzoylhydrazine.

Benzaldehyde (0.47 g.) was added to a warm ethanolic solution of *N*-(2-amino)phenyl-*N'*-benzoylhydrazine (13) (1 g. in 50 ml.), which was then refluxed for 15 minutes under nitrogen. After cooling, 0.6 g. of yellow crystals were obtained, which, after crystallization from ethanol, gave white needles melting at 149-150°; uv (ethanol): λ max nm (log ε) 254 sh (3.94), 302 (3.80).

Anal. Calcd. for $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43; N, 13.33. Found: C, 76.24; H, 5.46; N, 13.29.

Oxidation of *N*-(2-Benzylidenamino)phenyl-*N'*-benzoylhydrazine.

Air was bubbled for 24 hours through a solution of 0.5 g. of the above compound in ethanol-tetrahydrofuran (40 ml., 4/1, v/v). The solution was concentrated to a small volume, thus recovering 0.38 g. of starting material. The filtered solution was evaporated to dryness and the residue was chromatographed on alumina (activity I) eluting with dichloromethane. Additional 60 mg. of starting material were firstly recovered, followed by 40 mg. (~ 8%) of 1-benzoylamino-2-phenylbenzimidazole, m.p. and mixed m.p. 182-184°.

2-R'-Benzimidazoles.

Each of aldehyde 2-aminophenylhydrazones, just prepared as indicated above, was dissolved in ethanol (0.5 g. in 20 ml.). Concentrated hydrochloric acid (5 ml.) was added and the solution was left at room temperature for 24 hours under nitrogen in a well closed vessel. The solvent was removed under reduced pressure, water (5 ml.) was added and the solution was saturated with potassium carbonate, thus observing ammonia evolution (Nessler's test positive). The alkaline solution was extracted several times with dichloromethane and the combined extracts (~ 100 ml.) were dried, concentrated to small volume and then chromatographed on silic gel (80 g.). Eluting with dichloromethane, a small amount of impurities were eliminated firstly; then, using dichloromethane with 5% of methanol, the corresponding pure benzimidazoles were recovered. 2-Benzylbenzimidazole can be eluted with 1% methanol in dichloromethane. Yields of 2-R'-benzimidazoles were in the range from 67% to 86% of calculated values. The obtained benzimidazoles (VIIa-e) were identified through uv spectra (22,23) and mixed m.p. (24) with authentic samples.

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