Triazolines.† Part 32.[1] Synthesis of 1-Alkyl-2-aminobenzimidazoles from 5-Amino-1-(2-nitroaryl)-1,2,3-triazolines

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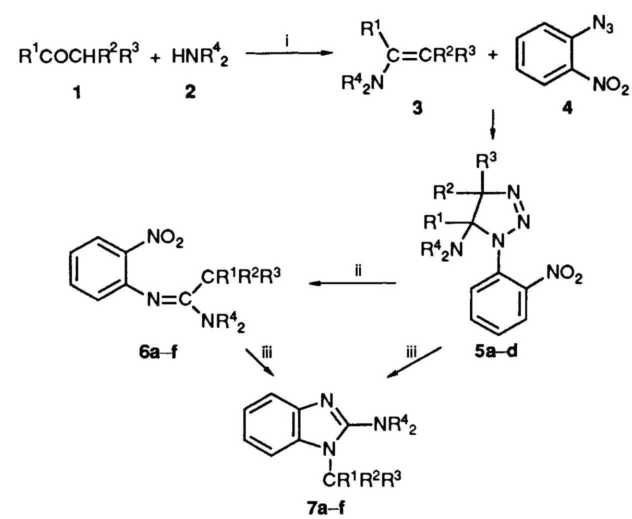
5-Amino-1-(2-nitroaryl)-1,2,3-triazolines **5** are converted into 1-alkyl-2-aminobenzimidazoles **7** in refluxing triethyl phosphite. The reaction occurs *via* thermal rearrangement of **5** followed by nitrogen elimination which produces N^2-(2-nitroaryl)amidines **6** as intermediates. Reduction of the nitro group to nitrene, addition to the C=N bond and rearrangement of the intermediate 2,2-disubstituted benzimidazoles accounts for the formation of the end products.

5-Amino-1-aryl-1,2,3-triazolines are readily available compounds which in most cases are obtained by [3 + 2]cycloaddition of azides to enamines.[2] Their ring easily undergoes a thermal fragmentation accompanied by nitrogen elimination and rearrangement giving access to nitrogen-containing products, mostly substituted amidines[3] which are well recognized synthons for the preparation of heterocyclic compounds. Despite this high synthetic potential, the use of 5-amino-1,2,3-triazolines in heterocyclic synthesis has not been fully explored.

As a part of a programme aiming to develop general syntheses of nitrogen-containing heterocycles from substituted 5-amino-1-aryl-1,2,3-triazolines we have now discovered a new and practical entry to 1-alkyl-2-aminobenzimidazoles starting from 1-(2-nitroaryl)-1,2,3-triazolines.



	R^1	R^2	R^3	NR^4_2
5, 6, 7a	H	Et	H	morpholino
b	H	Et	H	NMe_2
c	H	Me	H	morpholino
d	-$(CH_2)_4$-		H	morpholino
e	H	Me	Me	pyrrolidino
f	H	Ph	H	morpholino

Scheme 1 *Reagents and conditions:* i, PhH, room temp.; ii, heat; iii, $P(OEt)_3$, reflux

Results and Discussion

Triazolines **5a–d** are new compounds and were readily prepared according to a known procedure[4] (Scheme 1). Thus compounds **5a–c** were prepared by a one-pot reaction of the corresponding aldehyde **1** with a secondary amine **2** and an aryl azide **4** in inert solvent without isolation of the intermediate enamine deriving from the condensation of **1** and **2**. Compound **5d** was obtained from 1-morpholinocyclohexene and 2-nitrophenyl azide under similar conditions.

Compounds **5a–c** and **5g** show in their ^{1}H NMR spectra the expected signals, with correct multiplicities, in the ranges (δ 4.70–4.30 and 4.70–4.45) associated with 4-H and 5-H, respectively.[5] A vicinal coupling constant of 2.9–3.0 Hz indicates a *trans* configuration for **5a–c**.

5-Amino-1,2,3-triazolines bearing electron-withdrawing substituents at N-1 are known to be thermally labile compounds and in refluxing benzene the products **5a–d** were readily converted into the corresponding amidines **6a–d**. The triazolines formed from the enamines of isobutyraldehyde and phenylacetaldehyde were even more unstable, undergoing extensive rearrangement into the corresponding amidines **6e, f**, during their preparation. The isolation of these compounds was not, therefore, attempted and the transformation into **6** was completed by a short heating at 70–80 °C. The mechanism of the thermal rearrangement of 5-amino-1,2,3-triazolines has been already studied extensively.[2]

In an excess of refluxing triethyl phosphite, the triazolines **5a–d** were, with time, transformed in good yield into the corresponding benzimidazoles **7a–d**, respectively, which were readily isolated pure. The monitoring of the reaction course suggested that compounds **5a–d** were first converted into the amidines **6a–d** by a relatively quick reaction (typically in 15–30 min), during which the triethyl phosphite acts simply as high-boiling solvent. Compounds **6a–d** were then slowly (8–15 h) transformed into benzimidazoles **7a–d** through reduction of the nitro group by the triethyl phosphite, cyclization and rearrangement. In line with this, quenching of the reaction mixture after a short time (*ca.* 15 min) allowed isolation of the amidines **6a–d** practically as the sole reaction products. Benzimidazoles **7e, f** were obtained under similar conditions directly from the corresponding amidines **6e, f**.

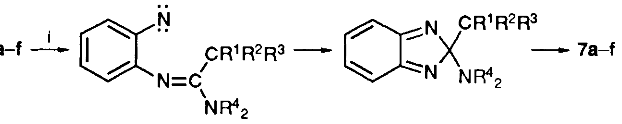
Structural assignments for the benzimidazoles **7a–f** were established mainly from ^{1}H NMR data. In all cases, besides the expected signals for the 2-amino substituent and the downfield shift of the alkyl groups with respect to the starting materials as consequence of the migration from carbon to nitrogen, a typical[6] pattern for the aromatic hydrogens was always observed; this was characterized by the lowfield signal associated with 4-H (δ 7.5–7.6).

Chemical confirmation for the structure of **7c** was further obtained by an independent synthesis starting from *N*-ethyl-

† 4,5-Dihydrotriazoles.

o-phenylenediamine through 1-ethylbenzimidazol-2-one, 2-chloro-1-ethylbenzimidazole and reaction with morpholine, according to a published synthetic process.[7]

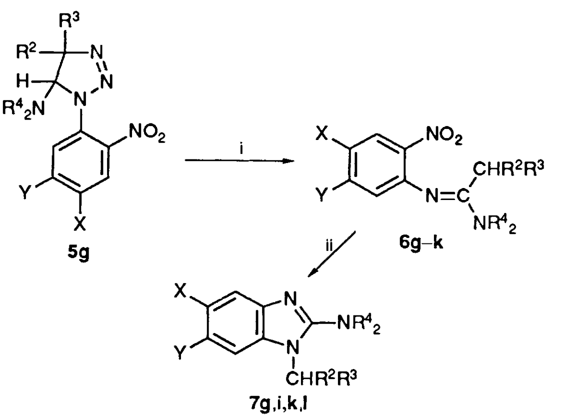
From a mechanistic point of view the foregoing results are rationalized as follows (Scheme 2). Reduction by triethyl



Scheme 2 *Reagent and conditions:* i, $P(OEt)_3$, reflux

phosphite of the nitro group is a well established way to generate a reactive nitrene intermediate.[8] From amidines **6a, f** isolated or formed *in situ* when triazolines **5** are used as starting materials, nitrenes are produced which rapidly undergo a cyclization by addition to the C=N double bond. 2,2-Disubstituted benzimidazoles (isobenzimidazoles) are so formed, which undergo a thermal [1.5]shift of the alkyl group toward nitrogen. This shift is probably also a quick reaction, at least in refluxing triethyl phosphite, since we were not able to identify these intermediates. A few examples of [1.5]shifts in 2,2-disubstituted imidazoles have been described.[9]

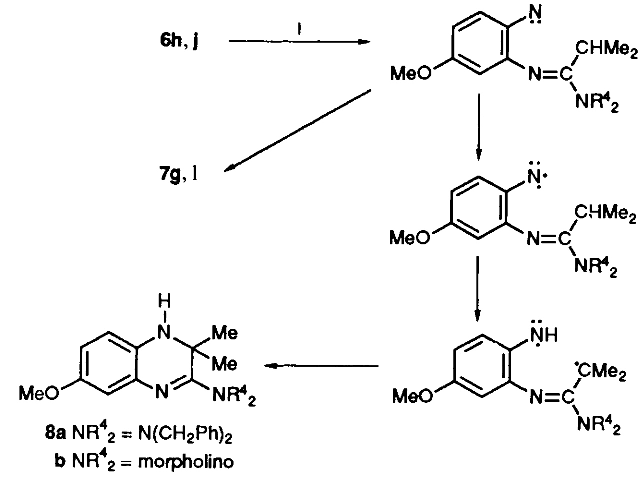
Scheme 3 depicts the results which were obtained from



	X	Y	R^2	R^3	NR^4_2
5, 6, 7g	MeO	H	Me	Me	$N(CH_2Ph)_2$
h	H	MeO	Me	Me	$N(CH_2Ph)_2$
i	MeO	H	Me	Me	morpholino
j	H	MeO	Me	Me	morpholino
k	Cl	H	H	Me	morpholino
l	H	Cl	H	Me	morpholino

Scheme 3 *Reagent and conditions:* i, heat; ii, $P(OEt)_3$, reflux

compounds **5g** and **6g–k** which are characterized by a further substituent on the phenyl ring. The starting materials were obtained as described above starting from the appropriate aldehyde, amine and aryl azide. Only the triazoline **5g** was stable enough for isolation. Prolonged heating in triethyl phosphite of the amidine **6k** resulted in a reaction mixture in which both isomeric **7k** and **7l** were present in nearly equimolar amounts. Enriched fractions (more than 90%) of both compounds could be prepared by column chromatography, but complete separation was not achieved. Clearly, in this case the intermediate isobenzimidazole (Scheme 2) gives rise to both the possible rearrangement products. A different result was obtained from **5g** (through the intermediacy of the amidine **6g**) and from **6i**. Both reactions produced a single compound in each instance, *i.e.* the corresponding 5-methoxybenzimidazoles **7g** and **7i**, respectively. On the other hand, both **6h** and **6j** under the same reaction conditions afforded a mixture of two products. The major one (*ca.* 95%) was identified as **7g** or **7i**, respectively, *i.e.* the same products formed from the isomeric starting materials **5g** and **6i**. In the ^{1}H NMR spectra of compounds **7g**, **i** the position of the methoxy group is confirmed by the presence of a highfield signal at δ 6.75–6.90; (dd, J_m 2.5, J_o 8.0 Hz) associated with 6-H and signals at δ 7.2 (d, J 2.5) and δ 7.3 (d, J 8.0) corresponding to 4-H and 7-H, respectively. The higher field shift of the signal associated with 4-H demonstrates its *ortho* relation with the methoxy group. These assignments were confirmed by a NOESYPH experiment on **7i** showing the expected effects between the signals associated with the methoxy group and the aromatic protons and, most relevant, an effect between the signal corresponding to the CH_3 groups and 7-H (δ 7.3). In the chloro substituted benzimidazoles **7k** and **7l** the shielding effect of the substituent is clearly absent. They are distinguished one from another since in the former the lowfield resonance associated with 4-H shows a *meta* coupling constant (1 Hz), whereas in the latter the corresponding signal is split by an *ortho* (8.4 Hz) coupling constant. To the by-products obtained from **6h** and **6j**, which could not be prepared in analytically pure form, the structure of 3-dibenzylamino- or 3-morpholino-6-methoxy-2,2-dimethyl-1,2-dihydroquinoxaline **8a** or **8b** was assigned on the basis of ^{1}H NMR evidence (importantly, δ 1.35–1.40, s, associated with the geminal Me groups, besides the expected signals for the amino group and aromatic protons). The different behaviour of compounds **6g**, **i** with respect to **6h**, **j** can be explained on the basis of the stabilizing effect exerted by the *p*-methoxy group on the nitrene species. This allows for partial transition to the triplet state (Scheme 4) which is responsible for hydrogen



Scheme 4 *Reagent and conditions:* i, $P(OEt)_3$, reflux

abstraction from the isopropyl group and formation of a diradical intermediate which undergoes cyclization to **8a**, **b**.[10]

Experimental

All aldehydes **1** were freshly distilled before use. M.p.s were performed with a Büchi 510 apparatus. NMR spectra were recorded on an Ac 200 Bruker spectrometer (^{1}H 200.13 MHz, ^{13}C 50.327 MHz) in $CDCl_3$ and chemical shifts are reported in ppm relative to Me_4Si as internal standard. IR spectra were recorded on a Jasco IR Report 100 instrument. Analytical and spectral data are reported in Table 1.

Preparation of 4-*Alkyl*-5-*amino*-1-(2-*nitroaryl*)-4,5-*dihydro*-1,2,3-*triazoles* **5a–c**, **g**. *General Procedure.*—A benzene solution (50–100 cm^3) of 2-nitroaryl azide **4** (30 mmol) was mixed with an equimolar amount of aldehyde **1**. Into the solution was

Table 1 Analytical and spectral data of compounds **5**, **6** and **7**

Compound (formula)	Yield (%)	M.p./°C (solvent)	δ_H (J/Hz)	Found (%) (Required) C	H	N
5a ($C_{14}H_{19}N_5O_3$)	92	134 (Pr^i_2O)	1.06 (3 H, t, Me, J 7.5), 1.64–1.80 (2 H, m, CH_2), 2.20–2.23 [4 H, m, $(CH_2)_2N$], 3.39–3.45 [4 H, m, $(CH_2)_2O$], 4.42–4.49 (2 H, m, 4-H, 5-H), 7.11–7.92 (4 H, m, Ar)	55.1 (55.06)	6.3 (6.27)	23.1 (22.94)
5b ($C_{12}H_{17}N_5O_2$)	85	Oil	1.05 (3 H, t, Me, J 6.3), 1.48–1.91 (2 H, m, CH_2), 1.97 (6 H, s, Me_2N), 4.32–4.40 (1 H, m, 4-H), 4.51 (1 H, d, 5-H, J 3), 7.18–7.90 (4 H, m, Ar)			
5c ($C_{13}H_{17}N_5O_3$)	68	114–114 (Pr^i_2O)	1.34 (3 H, d, Me, J 7.1), 2.21–2.25 [4 H, m, $(CH_2)_2N$], 3.40–3.49 [4 H, m, $(CH_2)_2O$], 4.43 (1 H, d, 5-H, J 3), 4.54 (1 H, dq, 4-H, J 7.1), 7.2–8.0 (4 H, m, Ar)	53.6 (53.61)	5.8 (5.84)	24.15 (24.05)
5d ($C_{16}H_{21}N_5O_3$)	68	132–134 (Pr^i_2O)	1.25–2.51 [12 H, m, $(CH_2)_4(CH_2)_2N$], 3.67–3.74 [4 H, m, $(CH_2)_2O$], 4.67 (1 H, t, 4-H, J 5.6), 7.16–8.16 (4 H, m, Ar)	57.8 (58.16)	5.8 (6.10)	20.9 (21.20)
5g ($C_{25}H_{27}N_5O_3$)	24	114 (Pr^i_2O)	1.15 (3 H, s, Me), 1.62 (3 H, s, Me), 3.35–3.66 [4 H, m, $(CH_2)_2$], 3.95 (3 H, s, MeO), 4.66 (1 H, s, 5-H), 7.1–7.8 (3 H, m, Ar)	67.3 (67.39)	5.9 (6.11)	15.4 (15.72)
6a ($C_{14}H_{19}N_3O_3$)	86	70 (Et_2O–pentane)	0.82 (3 H, t, Me, J 13), 1.38–1.58 (2 H, m, CH_2–Me), 2.16–2.25 (2 H, m, CH_2–C=), 3.50–3.55 [4 H, m, $(CH_2)_2N$], 3.72–3.77 [4 H, m, $(CH_2)_2O$], 6.78–7.93 (4 H, m, Ar)	61.0 (60.63)	7.0 (6.90)	15.4 (15.15)
6b ($C_{12}H_{17}N_3O_2$)	52	Oil	0.78 (3 H, t, Me, J 7.5), 1.35–1.51 (2 H, m, CH_2–Me), 2.15–2.23 (2 H, m, CH_2–C=), 2.99 (6 H, s, Me_2N), 6.75–7.86 (4 H, m, Ar)			
6c ($C_{13}H_{17}N_3O_3$)	64, 10[a]	Oil	1.04 (3 H, t, Me, J 7.7), 2.27 (2 H, q, CH_2, J 7.7), 3.51–3.56 [4 H, m, $(CH_2)_2N$], 3.73–3.78 [4 H, m, $(CH_2)_2O$], 6.79–7.93 (4 H, m, Ar)			
6d ($C_{16}H_{21}N_3O_3$)	73, 10[a]	Oil	1.41 [8 H, m, $(CH_2)_4$], 2.78–2.98 (1 H, m, CH), 3.43–3.52 [4 H, m, $(CH_2)_2N$], 3.70–3.82 [4 H, m, $(CH_2)_2O$], 6.72–7.95 (4 H, m, Ar)			
6e ($C_{14}H_{19}N_3O_2$)	45	Oil	1.16 (6 H, d, 2 Me, J 7), 1.85–1.88 [4 H, m, $(CH_2)_2$], 2.78–2.85 (1 H, m, CH=), 3.38–3.45 [4 H, m, $(CH_2)_2N$], 6.79–7.8 (4 H, m, Ar)			
6f ($C_{18}H_{19}N_3O_3$)	50	92–94 (Pr^i_2O)	3.48–3.59 [4 H, m, $(CH_2)_2N$], 3.61–3.63 [4 H, m, $(CH_2)_2O$], 3.71 (2 H, s, CH_2), 6.81–7.92 (9 H, m, Ar)	66.0 (66.44)	5.85 (5.88)	12.8 (12.91)
6g ($C_{25}H_{27}N_3O_3$)	41, 5[a]	Oil	0.86 (6 H, d, 2 Me, J 7.5), 3.01 (1 H, sept, CH, J 7.5), 3.83 (3 H, s, MeO), 4.63 [4 H, s, $(CH_2)_2N$], 6.71–7.51 (13 H, m, Ar)			
6h ($C_{25}H_{27}N_3O_3$)	40	81–83 (pentane)	1.20 (6 H, d, 2 Me, J 7.2), 3.00 (1 H, sept, CH, J 7.2), 3.81 (3 H, s, MeO), 4.63 [4 H, s, $(CH_2)_2N$], 6.15–8.07 (13 H, m, Ar)	71.7 (71.92)	6.4 (6.52)	9.9 (10.06)
6i ($C_{15}H_{21}N_3O_4$)	53	Oil	1.16 (6 H, d, 2 Me, J 7.3), 2.86 (1 H, 5, CH, J 7.3), 3.47–3.52 [4 H, m, $(CH_2)_2N$], 3.71–3.81 [4 H, m, $(CH_2)_2O$], 3.81 (3 H, s, MeO), 6.68–7.44 (3 H, m, Ar)			
6j ($C_{15}H_{21}N_3O_4$)	47	100–101 (Pr^iOH)	1.17 (6 H, d, 2 Me, J 7.3), 2.86 (1 H, sept, CH, J 7.3), 3.49–3.53 [4 H, m, $(CH_2)_2N$], 3.36–3.77 [4 H, m, $(CH_2)_2O$], 3.83 (3 H, s, MeO), 6.20–8.02 (3 H, m, Ar)	58.55 (58.61)	6.7 (6.88)	13.75 (13.67)
6k ($C_{13}H_{16}ClN_3O_3$)	59, 10[a]	Oil	1.03 (3 H, t, Me, J 7.6), 2.25 (2 H, q, CH_2, J 7.6), 3.39–3.65 [4 H, m, $(CH_2)_2N$], 3.71–3.92 [4 H, m, $(CH_2)_2O$], 6.74–7.90 (3 H, m, Ar)			
7a ($C_{14}H_{19}N_3O$)	73	65 (pentane)	0.94 (3 H, t, Me, J 7.5), 1.77–1.96 (2 H, m, CH_2–Me), 3.26–3.30 [4 H, m, $(CH_2)_2N$], 3.86–4.01 [6 H, m, $(CH_2)_2O$, CH_2N], 7.15–7.28 (3 H, m, Ar), 7.52–7.65 (1 H, m, 4-H)	68.55 (68.54)	7.8 (7.80)	16.9 (17.13)
7b ($C_{12}H_{17}N_3$)	60	Oil	0.95 (3 H, t, Me, J 7.5), 1.85 (2 H, tq, CH_2, J 7.5, 8.57), 2.96 (6 H, s, Me_2N), 3.96 (2 H, t, CH_2N, J 8.57), 7.13–7.21 (3 H, m, Ar), 7.49–7.60 (1 H, m, 4-H)			
7c ($C_{13}H_{17}N_3O$)	62	95–96 (pentane)	1.46 (3 H, t, Me, J 7.2), 3.28–3.33 [4 H, m, $(CH_2)_2N$], 3.86–3.91 [4 H, m, $(CH_2)_2O$], 4.08 (2 H, CH_2, J 7.2), 7.12–7.34 (3 H, m, Ar), 7.58–7.67 (1 H, m, 4-H)	67.15 (67.50)	7.5 (7.41)	17.6 (18.16)
7d ($C_{16}H_{21}N_3O$)	60	125–126 (pentane)	1.75–2.29 [8 H, m, $(CH_2)_4$], 3.23–3.28 [4 H, m, $(CH_2)_2N$], 3.87–3.92 [4 H, m, $(CH_2)_2O$], 4.77, 4.86 (1 H, m, CHN), 7.12–7.34 (3 H, m, Ar), 7.63–7.67 (1 H, m, 4-H)	70.6 (70.86)	7.8 (7.99)	15.5 (15.14)
7e ($C_{14}H_{19}N_3$)	83	Oil	1.59 (6 H, d, 2 Me, J 6.9), 1.94–2.00 [4 H, m, $(CH_2)_2$], 3.52–3.57 [4 H, m, $(CH_2)_2N$], 4.69 (1 H, sept, CH, J 6.9), 6.98–7.41 (3 H, m, Ar), 7.50–7.60 (1 H, m, 4-H)			
7f ($C_{18}H_{19}N_3O$)	95	125 (pentane)	3.23–3.27 [4 H, m, $(CH_2)_2N$], 3.79–3.83 [4 H, m, $(CH_2)_2O$], 5.25 (2 H, s, CH_2–Ph), 7.00–7.42 (8 H, m, Ar), 7.64 (1 H, m, 4-H)	73.5 (73.69)	6.7 (6.53)	14.4 (14.32)
7g ($C_{25}H_{27}N_3O$)	69	Oil	1.32 (6 H, d, 2 Me, J 6.9), 3.84 (3 H, s, MeO), 4.30 [4 H, s, $(CH_2)_2$], 4.87 (1 H, sept, CH, J 6.9), 6.75–6.88 (1 H, dd, 6-H), 7.21–8.10 (12 H, m, Ar)			
7i ($C_{15}H_{21}N_3O_2$)	65	160–161 (Pr^i_2O)	1.57 (6 H, d, 2 Me, J 6.9), 3.18–3.25 [4 H, m, $(CH_2)_2N$], 3.83 (3 H, s, MeO), 3.86–3.91 [4 H, m, $(CH_2)_2O$], 4.56 (1 H, sept, CH, J 6.9), 6.75 [1 H, dd, 6-H, J_m 2.5, J_o 8.0), 7.19 (1 H, d, 4-H, J_m 2.5), 7.29 (1 H, d, 7-H, J_o 8.0)	65.1 (65.42)	7.7 (7.68)	15.0 (15.26)
7k ($C_{13}H_{16}ClN_3O$)	71[b]		1.44 (3 H, t, Me, J 7.3), 3.27–3.33 [4 H, m, $(CH_2)_2N$], 3.87–3.91 [4 H, m, $(CH_2)_2O$], 4.05 (2 H, q, CH_2, J 7.3), 7.12–7.25 (2 H, m, 6-H, 7-H), 7.58 (1 H, d, 4-H, J 1.0)	58.5 (58.74)	6.3 (6.07)	15.5 (15.81)[c]
7l ($C_{13}H_{16}ClN_3O$)			1.45 (3 H, t, Me, J 7.2), 3.24, 3.31 [4 H, m, $(CH_2)_2N$], 3.87–3.91 [4 H, m, $(CH_2)_2O$], 4.04 (2 H, q, CH_2, J 7.2), 7.18 (1 H, dd, 5-H, J_o 8, J_m 1.2), 7.23 (1 H, d, 7-H, J 1.9), 7.50 (1 H, d, 4-H, J_o 8)			

[a] Second figure indicates yield of **6** as a by-product in the preparation of **7**. [b] Total yield of isomers. [c] Analytical data of a purified mixture of isomers.

dropped the amine **2** (30 mmol) at room temperature. The reaction mixture was stirred for 2–14 h until disappearance of the starting materials (TLC, eluent 40% ethyl acetate–cyclohexane). The solution was dried (Na_2SO_4), filtered, evaporated to dryness and the residue crystallized with the solvent indicated in Table 1. For **5b**, **g** the crude reaction product was purified by chromatography on neutral aluminium oxide with 30% ethyl acetate–cyclohexane as the eluent.

Thermal Decomposition of Compounds **5a–d**. *General Procedure.*—Purified compound **5** (10 mmol) was dissolved in boiling toluene (20 cm^3). The solution was refluxed for 1–5 h until disappearance of **5** and then evaporated to dryness under reduced pressure. Crude product **6a** was directly crystallized, whereas **6b–d** were purified by chromatography on a silica gel column (eluent 20% ethyl acetate–cyclohexane) and used without further purification for the subsequent reaction.

Preparation of the Amidines **6e–k**.—A benzene solution (50–100 cm^3) of 2-nitroaryl azide **4** (30 mmol) was mixed with an equimolar amount of aldehyde **1**. To the solution was added the amine **2** (30 mmol). The mixture was refluxed for 30–60 min until complete transformation into the amidine **6** (TLC, 40% ethyl acetate–cyclohexane as eluent). The solution was dried (Na_2SO_4), filtered and evaporated to dryness. The crude residue was chromatographed on a silica gel column with 30% ethyl acetate–cyclohexane and the major fraction crystallized with the solvent indicated in Table 1. The oily amidines **6e**, **i**, **k** were used without further purification for the subsequent reaction.

Preparation of Compound **5d**.—To a benzene solution (130 cm^3), of 2-nitrophenylazide (10.0 g, 59 mmol) was added 1-morpholinocyclohexene (9.8 g, 59 mmol). The solution was refluxed for 15 min and evaporated to dryness. The yellow oil crystallized upon addition of diisopropyl ether.

Reaction of Compounds **5** *or* **6** *with Triethyl Phosphite: General Procedure.*—A mixture of **5** or **6** (10 mmol) in triethyl phosphite (20 cm^3) was refluxed under inert atmosphere for 10–30 h. When the amidine was no longer detectable in substantial amounts (TLC, 40% ethyl acetate–cyclohexane) the solution was evaporated under reduced pressure and the crude residue chromatographed on a silica gel column with 40% ethyl acetate–cyclohexane. Two fractions were usually collected; a first minor fraction containing the unchanged amidine **6**, and a second fraction containing the benzimidazole **7**.

Independent Synthesis of Compound **7c**.—Under N_2, *N*-ethyl-*o*-phenylenediamine (6.7 g, 45.9 mmol) was mixed with urea (4.1 g, 68.0 mmol). The mixture was heated at 180 °C for 16 h. The crude residue was taken up with 50% ethyl acetate–cyclohexane yielding 1-ethylbenzimidazol-2-one (3.7 g, 41%), m.p. 117–18 °C (Found: C, 66.4; H, 6.3; N, 17.1. $C_9H_{10}N_2O$ requires: C, 66.64; H, 6.21; N, 17.27); ν_{max}(Nujol)/cm^{-1} 1700 (C=O); δ_H 1.38 (3 H, t, CH_3, *J* 8.8), 3.97 (2 H, q, CH_2, *J* 8.8), 6.99 (4 H, m, Ar). A mixture of 1-ethylbenzimidazol-2-one (2 g, 12 mmol) and $POCl_3$ (5 cm^3) was heated at 140 °C for 4 h. The crude residue was poured into ice (40 g), neutralized with $NaHCO_3$ and extracted with benzene. The organic layers, dried (Na_2SO_4), were evaporated to dryness, giving a viscous oil of 2-chloro-1-ethylbenzimidazole which was not purified further (yield 2.0 g, 90%); ν_{max}/cm^{-1} 1710 (C=N); δ_H 1.41 (3 H, t, CH_3, *J* 7.12), 4.26 (2 H, q, CH_2, *J* 7.12), 7.22–7.35 (3 H, m, Ar), 7.65–7.71 (1 H, m, 4-H). A solution of 2-chloro-1-ethylbenzimidazole (2.0 g, 16 mmol) and morpholine (1.4 g, 16 mmol) in ethanol (10 cm^3) was heated at 150–160 °C under pressure for 16 h. After evaporation the crude residue was basified with 5% NaOH, extracted with ethyl ether and dried with Na_2SO_4. The residue, after evaporation, was crystallized from light petroleum (b.p. 40–60 °C) (yield 0.7 g, 19%), m.p. 95 °C.

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