N-Halogenoamidines. Part 1. Amino-imidazolines and -imidazoles from *N*-Chloro-*N'*-arylamidines and Enamines

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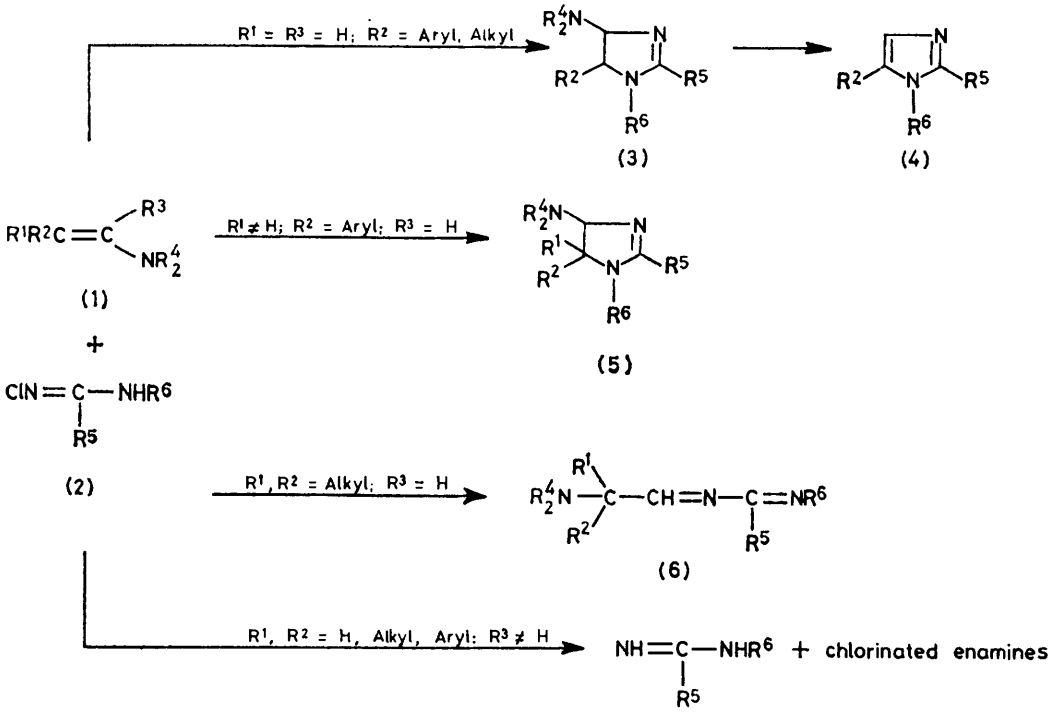
The reaction between *N*-chloro-*N'*-arylamidines and enamines derived from aldehydes affords 4-amino-4,5-dihydro-imidazoles and/or -imidazoles. Imidazole-ring formation was not observed with enamines from ketones and from aldehydes bearing two alkyl groups in the β-position. In the former case chlorinated enamines were obtained, and in the latter a rearrangement to *N*-(2-amino-2,2-dialkyl)ethylidene-amidines was observed. The reaction mechanism is discussed.

A PRELIMINARY report of the synthesis of the imidazole ring by reaction of *N*-chloro-*N'*-arylamidines with enamines has appeared.[1] Here we report the results obtained for the reaction of *N*-chloroamidines of the general formula (2) and enamines (1).



SCHEME 1

Since it is known that the reactions of enamines are strongly dependent upon the substituents on the double bond,[2] several substitution patterns have been considered in this study. The reaction was generally carried out in $CHCl_3$ or in CH_2Cl_2 in the presence of an equimolecular amount of pyridine.

As shown in Scheme 1, the substituents on the enamine double-bond play an important role on the reaction course.

When $R^1 = R^2 = H$ (*i.e.* in the case of the enamines from α-unbranched aldehydes) the corresponding imidazoles (4) (Table 1) were directly obtained. In most cases the intermediate 4-amino-4,5-dihydroimidazoles were not isolated, owing to their ready aromatisation. However, by careful work-up of the reaction mixture from β-morpholinostyrene and the chloroamidines (2a) and (2c) (Table 4) the imidazolines (3a) and (3b) (Table 2) were obtained besides the corresponding imidazoles (4a) and (4d). Compounds (3a) and (3b) readily deaminate to give the imidazoles (4a) and (4d) when heated in the presence of pyridine·HCl or triethylamine·HCl.

The reaction between *N*-chloroamidines (2) and enamines is not significantly influenced by the amine residue in the enamine. The imidazole (4a) was obtained almost in the same yield from β-morpholino-, β-pyrrolidino-, β-piperidino-, and β-(*N*-methyl anilino)-styrene.

In all cases only one imidazole product was found and this supports the regiospecificity of the reaction.

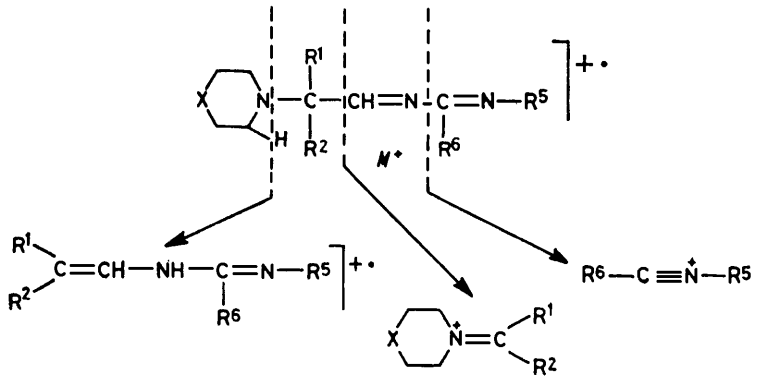
The structure of 1,2,5-trisubstituted imidazoles was

[1] D. Pocar, R. Stradi, and B. Gioia, *Tetrahedron Letters*, 1976, **21**, 1839.
[2] J. Szmuskowicz, *Adv. Org. Chem.*, 1963, **4**, 1.

assigned to the products on the basis of the spectroscopic and mass spectrometric data. Moreover, the imidazole (4a) was found to be identical with an authentical sample.[3]

Essentially the same behaviour was observed in the case of the enamines in which $R^1 \neq H$, R^2 = aryl, and R^3 = H. They reacted with *N*-chloroamidines yielding the expected imidazolines (5a—i). Owing to the presence of two substituents in the 4-position, which hinders the amine elimination, these compounds show a remarkable stability and could easily be isolated in good yield.

Clearly, the anisotropic effect exerted by the aromatic ring on the morpholino-group must be different for the *E*- and *Z*-isomers. The molecular models show that the morpholino-methylene groups are included in the shielding zone of the phenyl ring; accordingly an upfield shift would be expected for these protons. This effect is clearly evidenced by the spectrum of the 5,5-diphenyl-substituted compound (5a) in which the signals associated with the morpholine group are found at δ 2.58 ($N[CH_2]_2$) and δ 3.33 ($O[CH_2]_2$), *i.e.* significantly upfield of the normal values (δ *ca.* 2.85 and *ca.* 3.75 respectively).



SCHEME 2

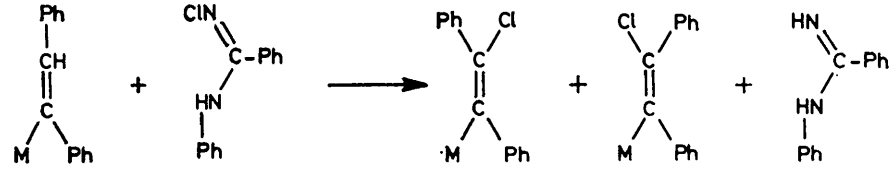
Also for this series of imidazolines (5a—i) the reaction was found to take a regiospecific course, only one product being isolated in each case. The structure of 4-amino-5,5-disubstituted-imidazolines was substantiated by its mass spectrum which was in good agreement with the known fragmentation pattern of this class of heterocycles.[4]

All the imidazolines isolated (3a—b) and (5a—i) were shown to be configurationally pure isomers. The *E*-configuration of the imidazolines (3a) and (3b) was inferred from the magnitude of $J_{4,5} = 4$ Hz which agrees with the Karplus rule for the above configuration. This assignment is in line with the values found for 5-amino-*v*-triazolines [$J_{4,5}(E) = 3$ Hz; $J_{4,5}(Z) = 9$ Hz].[5]

For the imidazolines (5a—i) the ^1H n.m.r. configurational assignments were based on the chemical-shift analysis alone. All the imidazolines prepared contained 4-morpholino- and 5-phenyl substituents.

The same effect has been observed for the *Z*-isomer of 2-methyl-3-morpholino-5-nitro-2-phenyl-2,3-dihydroindole in which the morpholino-signals were found at δ 2.30 and 3.20, whereas in the *E*-isomer the same protons resonate at the normal values of δ 2.75 and 3.75.[6]

In the series of imidazolines (5b—i) the morpholine protons resonate in the ranges of δ 2.75—2.85 and 3.70—3.78, as do the morpholine protons of the imidazolines (3a) and (3b). On this basis the *E*-configuration was assigned to these compounds.



M = morpholino

Reaction of 1-morpholino-2,2-diphenylethylene and *N*-chlorobenzamidine (2a), gave, besides the imidazoline (5a), a yellow by-product (6a). This was identified as *N*-(2-morpholino-2,2-diphenyl)ethylidene-*N'*-phenylbenzamidine on the basis of analytical and spectral data.

Two analogous products (6b) and (6c) were also found in the reaction mixtures from 1-morpholino-2-phenylpropene and *N*-chlorobenzamidine (2c), and from 1-

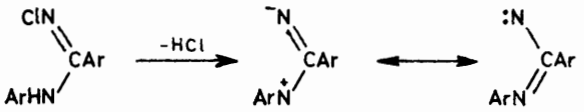
[3] H. A. Houwing, J. Wildeman, and A. M. Van Leusen, *Tetrahedron Letters*, 1976, **2**, 143. We thank Dr. H. A. Houwing who kindly communicated to us the results of this comparison.

[4] M. Ohashi, N. Ohno, H. Kakisawa, and A. Tatematsu, *Org. Mass Spec.*, 1968, **1**, 703.

[5] R. Stradi, D. Pocar, and G. Bianchetti, *Org. Mag. Res.*, 1972, **4**, 247.

[6] A. Diana, Thesis, Facoltà di Farmacia della Universita di Milano, 1976.

morpholino-2-(4-bromophenyl)propene and *N*-chloroamidine (2a) besides the expected imidazolines (5b) and (5h).



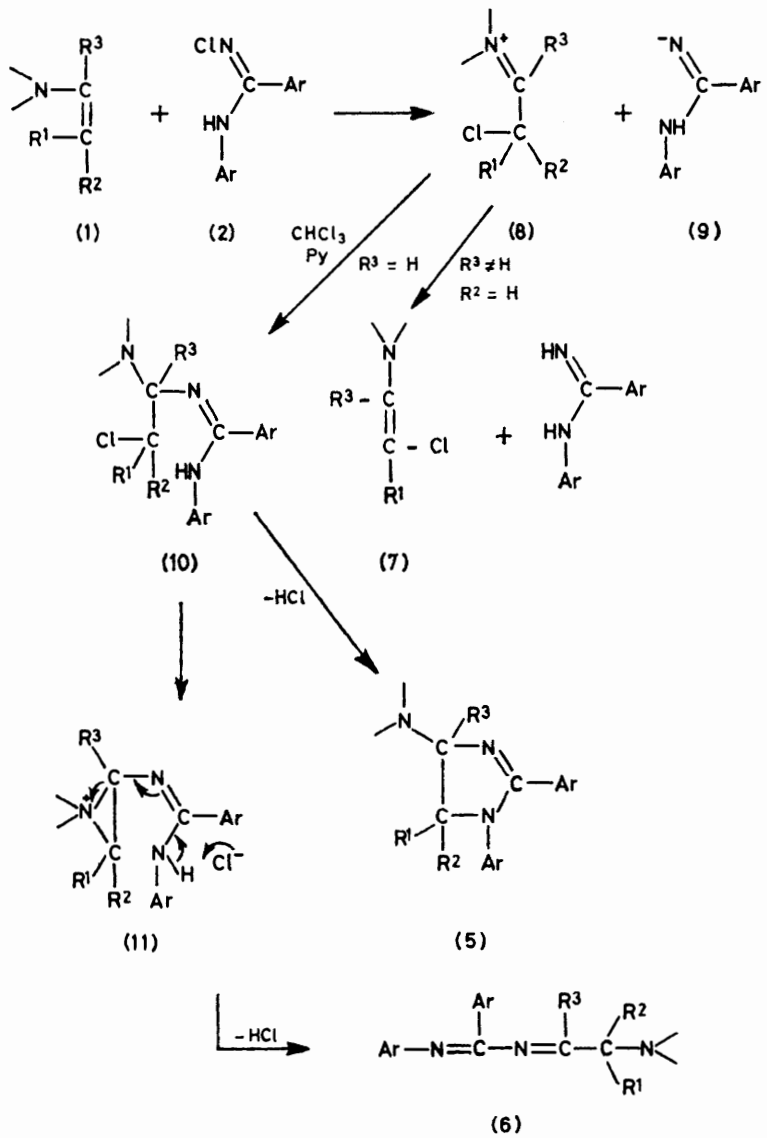
SCHEME 3

Compounds of the general formula (6) (Table 3) were obtained as the sole reaction product from the enamines starting from 1-morpholino-, -pyrrolidino-, and -piperidino-2-methylpropene.

The mass spectra of compounds (6e—g) show a weak molecular ion and the ions associated to the fragmentation pattern depicted in Scheme 2. The loss of amino-group from the molecular ion is probably due to a McLafferty-type mechanism.

When $R^3 \neq H$, *i.e.* in the cases of enamines from ketones, the formation of the imidazole ring was not observed, the reaction affording only chlorinated products derived from the enamine and the corresponding amidine.

On careful work-up of the reaction solution from



SCHEME 4

in which R^1, R^2 = alkyl and R^3 = H. This behaviour was found to be independent of the amino-group in the enamine. Essentially the same products were obtained

* S. J. Huang and M. V. Lessard [7] obtained the same equilibrium mixture ($Z : E = 3 : 2$) on chlorination of morpholino-stilbene with *N*-chlorosuccinimide.

morpholino-stilbene an equilibrium mixture of the *Z*- and *E*-isomers of chloro(morpholino)stilbene was isolated,* besides the *N*-phenylbenzamidine.

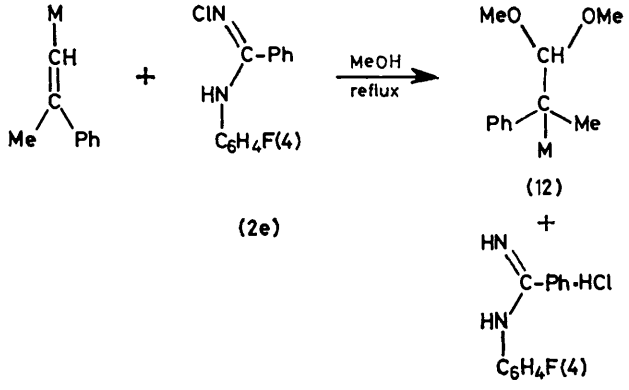
[7] S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, 1968, **90**, 2432.

DISCUSSION

In a preliminary paper [1] dealing with this reaction the formation of products (6) and (5) was tentatively explained by nitrene insertion and 1,3-dipolar cycloaddition, respectively, of the dehydrochlorination product of the *N*-chloroamidine (Scheme 3).

The results now available exclude this mechanism and suggest that in all cases the first stage of the reaction between *N*-chloroamidines and enamines is the direct electrophilic attack of the *N*-chloroamidine upon the unsaturated system of the enamine. An intermediate chloro–immonium ion is so formed which evolves in different ways as outlined in Scheme 4.

The main reaction is the nucleophilic attack of the amidine anion * (9) leading to the intermediate (10). This compound evolves to (5) or rearranges to (6) *via* the aziridinium chloride (11). As observed, the cyclization of (10) to (5) is preferred when the chloro-substituted carbon has benzylic character (R^1 and/or R^2 = Ar). In the case of enamines which derive from ketones ($R^3 \neq H$) the nucleophilic attack of (9) is sterically hindered, this making easier the deprotonation of the chloro-immonium ion (8) to the β-chloro-enamine (7). The above mechanism is supported by the following: (i) when 1-morpholino-2-phenylpropene was allowed to react with the chloro-amidine (2e) in boiling methanol



M = morpholino

SCHEME 5

instead of chloroform, the imidazoline (5i) was not formed and two products were isolated in almost quantitative yields: the *N*-(4-fluorophenyl)benzamidine hydrochloride and the 1,1-dimethoxy-2-morpholino-2-phenylpropane (12) (Scheme 5).

This compound is the expected product of the nucleophilic attack of methanol on the chloro-immonium ion (8) as shown by Duhamel *et al.*[8]

(ii) When the progress of the reaction of *N*-chloroamidine (2e) and 1-morpholino-2-phenylpropene was followed by ^1H n.m.r. spectroscopy the disappearance of the enamine within a few minutes could be established. However, the signals associated with imidazoline (5i) became clearly evident only after several hours at the operative temperature. During this time interval the spectrum showed signals which did not disagree with those expected for the intermediate (10).

EXPERIMENTAL

N.m.r. spectra were recorded on a Varian A-60 spectrometer at 60 MHz with $SiMe_4$ as internal standard and mass spectra on a Perkin-Elmer 270 mass spectrometer using the direct inlet technique, with a probe temperature of 120—140 °C; t.l.c. was run on silica gel GF 254 with benzene (50—80%)–tetrahydrofuran as eluant. M.p.s are uncorrected.

Enamines.—β-Morpholinostyrene,[9] β-piperidinosytrene,[10] β-pyrrolidinostyrene,[11] β-*N*-methylanilinostyrene,[12] 1-morpholino-2-methylpropene,[13] 1-piperidino-2-methylpropene,[11] 1-pyrrolidino-2-methylpropene,[14] 1-diethylaminobutene,[15] 1-morpholino-2-phenylpropene,[16] 1-morpholino-2,2-diphenylethene,[17] 1-morpholinostilbene,[18] and morpholinomethylidene-cyclohexane [19] are known compounds and were prepared by several methods.

In this work the enamines derived from phenyl acetaldehyde and from 2-phenylpropionaldehydes were all prepared from a mixture of the aldehyde and the amine (mol. ratio 1 : 3) the water produced being continuously distilled off with the benzene employed as solvent. The enamines from isobutyraldehyde were prepared by the method reported by Benzing [20] and finally the 1-diethylaminobutene by the method of White and Weingarten.[21]

Amidines.—*N*-Phenylbenzamidine, *N*-benzylbenzamidine,[22] *N*-(4-nitrophenyl)benzamidine, *N*-(*p*-tolyl)benzamidine, *N*-phenylacetamidine,[23] *N*-(4-bromophenyl)benzamidine,[24] *N*-(4-methoxyphenyl)benzamidine,[25] *N*-(4-fluorophenyl)benzamidine, and *N*-phenyl-4-bromobenzamidine [26] are known compounds and were prepared in different ways. The standard method described for *N*-phenylbenzamidine [27] was followed in order to prepare all the amidines employed in this work.

N-Chloroamidines (2).—To a solution of amidine (0.1

* For this anion two tautomeric forms can be formulated. The structure depicted has been chosen in line with the accepted formulation of *N*-chloro-*N'*-phenylamidines.

[8] L. Duhamel and J. M. Poirier, *Bull. Soc. chim. France*, 1975, 329.
[9] W. Ziegenbein and W. Franke, *Chem. Ber.*, 1957, **90**, 2291.
[10] C. Mannich and H. Davidsen, *Chem. Ber.*, 1936, **69**, 2106.
[11] H. Boehme and G. Berg. *Chem. Ber.*, 1966, **99**, 2127.
[12] J. Hoch, *Compt. rend.*, 1935, **200**, 938.
[13] P. L. De Benneville and J. H. Macartney, *J. Amer. Chem. Soc.*, 1950, **72**, 3073.
[14] G. Opitz and A. Grilsinger, *Annalen*, 1963, **665**, 101.
[15] P. Wittig and R. Mayer, *Z. Chem.*, 1967, **7**(2), 57.
[16] L. Duhamel, P. Duhamel, S. Combrisson, and P. Siret, *Tetrahedron Letters*, 1972, **34**, 3603.
[17] G. P. Hager and K. H. Stahl, *J. Amer. Pharm. Assoc.*, 1953, **42**, 72.
[18] M. E. Munk and Y. K. Kim, *J. Org. Chem.*, 1965, **30**, 3705.
[19] R. Noyori, K. Yokoyama, S. Hakino, and Y. Haiakawa, *J. Amer. Chem. Soc.*, 1972, **94**, 1772.
[20] E. Benzing, *Angew. Chem.*, 1959, **71**, 521.
[21] W. A. White and H. Weingarten, *J. Org. Chem.*, 1967, **32**, 213.
[22] P. Oxley, M. W. Partridge, and W. F. Short, *J. Chem. Soc.*, 1947, 1112.
[23] P. Oxley and W. F. Short, *J. Chem. Soc.*, 1946, 147.
[24] P. Oxley and W. F. Short, *J. Chem. Soc.*, 1949, 449.
[25] M. Osone, S. Tanimoto, and R. Oda, *Yuki Gosei Kagaku Shi*, 1966, **24**(7), 562.
[26] S. Robev, *Doklady Bolg. Akad. Nauk*, 1968, **21** (11), 1181.
[27] F. C. Cooper and M. W. Partridge, *Org. Synth.*, 1956, **36**, 64.

mol) in dry dichloromethane (100 ml), *N*-chlorosuccinimide (0.105 mol) was added. The mixture was stirred at room temperature for 2 h, and then washed twice with water. The organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure to give compound (2) (Table 4).

Reaction of the Enamines (1) *with* N-*Chloroamidines* (2): *General Procedure.*—To a solution of the enamine (1) (0.01 mol) and dry pyridine (0.88 g, 0.011 mol) in dry chloroform (50 ml) the *N*-chlorobenzamidine (2) (0.01 mol) was added.

The reaction mixture was refluxed until no more chloroamidine was detected by t.l.c., and was then cooled to room temperature and washed with a saturated $NaHCO_3$ solution. The organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure to give a crude reaction residue from which the reaction products were separated by column chromatography using benzene–tetrahydrofuran (85—15) as eluent. In some cases, chiefly for the imidazoles (4), the main reaction product crystallized out when the reaction mixture was set aside and could be purified by simple crystallization from a suitable solvent (Tables 1 and 2).

Reaction of 1-*Morpholinostilbene with* N-*Chloro*-N'-*phenylbenzamidine* (2a).—To a solution of 1-morpholinostilbene (2.65 g, 0.01 mol) and dry pyridine (0.8 g, 0.01 mol) in chloroform (50 ml), *N*-chloroamidine (2a) (2.35 g, 0.01 mol) was added. The reaction mixture was heated under reflux until no more enamine was detected by g.l.c. (*ca.* 1 h). The reaction solution (5 ml) was freed from solvent at room temperature under reduced pressure (0.1 Torr) and the crude residue extracted several times with dry benzene. The benzene solution was freed from solvent at reduced pressure at room temperature and the oily residue dissolved in $CDCl_3$ (1 ml). The n.m.r. spectrum [δ($CDCl_3$) 2.5 and 3.4 (morpholine-hydrogens of the *E*-isomer), 3.03 and 3.6 (morpholine-hydrogens of the *Z*-isomer), and 6.7—7.7 (aromatic)] allows an identification of the crude extract as a mixture of *Z*- and *E*-2-chloro-1-morpholinostilbene.[7]

Reaction of N-*Chloro*-N'-(4-*fluorophenyl*)*benzamidine* (2e) *and* 1-*Morpholino*-2-*phenylpropene in Methanol.*—To a

TABLE 1

Imidazoles

Product (4)	R^2	R^5	R^6	M.p. (°C)	Cryst. solvent	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
a	Ph	Ph	Ph	250 *	Ethanol	65	84.85	5.3	9.35	$C_{21}H_{16}N_2$	85.11	5.44	9.45
b	Ph	Ph	4-$NO_2C_6H_4$	270	Propan-2-ol	60	73.6	4.45	12.3	$C_{21}H_{15}N_3O_2$	73.89	4.43	12.31
c	Ph	Ph	4-$MeOC_6H_4$	221	Ethanol	40	80.9	5.35	8.55	$C_{22}H_{18}N_2O$	80.95	5.56	8.58
d	Ph	Ph	4-BrC_6H_4	218	Ethanol	55	67.4	4.1	7.6	$C_{21}H_{15}BrN_2$	67.20	4.02	7.46
e	Ph	Ph	4-FC_6H_4	243	Benzene	70	80.0	4.95	8.8	$C_{21}H_{15}FN_2$	80.23	4.80	8.91
f	Ph	4-BrC_6H_4	Ph	222	Ethanol	45	67.8	4.0	7.45	$C_{21}H_{15}BrN_2$	67.20	4.02	7.46
g	Ph	Me	Ph	122	Light petroleum	25	81.95	5.85	11.75	$C_{16}H_{14}N_2$	82.01	6.02	11.95
h	Et	Ph	4-FC_6H_4	109	Isopropyl ether	35	76.9	5.8	10.35	$C_{17}H_{15}FN_2$	76.66	5.67	10.52
i	Ph	Ph	$PhCH_2$	144	Isopropyl ether	40	85.4	5.75	8.9	$C_{22}H_{18}N_2$	85.13	5.85	9.03

* Ref. 3 quotes 251—252 °C.

TABLE 2

4-Morpholino-4,5-dihydroimidazoles

Product	R^1	R^2	R^4	R^6	M.p. (°C)	Cryst. solvent	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N	M^+ (*m/e*)	N.m.r. ($CDCl_3$) δ_{H_4}	δ_{H_5}
(3a)	H	Ph	Ph	Ph	202	EtOH	15	78.5	6.5	10.85	$C_{25}H_{25}N_3O$	78.30	6.57	10.96	383	4.72	4.72
																$J_{4,5}$ = 4Hz(*)	
(3b)	H	Ph	Ph	4-BrC_6H_4	197	EtOH	12	65.0	5.1	9.2	$C_{25}H_{24}BrN_3O$	64.93	5.23	9.08	461 463	4.69 or 4.71	4.69 or 4.71
																$J_{4,5}$ = 4Hz(*)	
(5a)	Ph	Ph	Ph	Ph	166	Pr^i_2O	55	80.7	6.35	9.2	$C_{31}H_{29}N_3O$	81.01	6.36	9.14	459	5.48	
(5b)	Me	Ph	Ph	Ph	182	Pr^i_2O	60	78.4	6.9	10.3	$C_{26}H_{27}N_3O$	78.56	6.85	10.57	397	4.62	
(5c)	Et	Ph	Ph	Ph	138	Pr^i_2O	35	78.5	7.2	10.05	$C_{27}H_{29}N_3O$	78.80	7.10	10.21	411	4.90	
(5d)	Me	Ph	Ph	4-$MeOC_6H_4$	202	Propan-2-ol	30	75.65	6.65	9.95	$C_{27}H_{29}N_3O_2$	75.85	6.84	9.83	427	4.60	
(5e)	Me	Ph	Ph	4-$NO_2C_6H_4$	255	EtOH	50	70.4	5.85	11.65	$C_{26}H_{26}N_4O_3$	70.57	5.92	12.66	442	4.67	
(5f)	Me	4-BrC_6H_4	Ph	Ph	125	Pr^i_2O	65	65.65	5.4	8.7	$C_{26}H_{26}BrN_3O$	65.54	5.50	8.82	475 477	4.51	
(5g)	Me	Ph	Ph	4-BrC_6H_4	240	EtOAc	70	65.2	5.65	8.7	$C_{26}H_{26}BrN_3O$	65.54	5.50	8.82	475 477	4.63	
(5h)	Me	Ph	4-BrC_6H_4	Ph	160	Pr^i_2O	65	65.3	5.35	8.7	$C_{26}H_{26}BrN_3O$	65.54	5.50	8.82	475 477	4.60	
(5i)	Me	Ph	Ph	4-FC_6H_4	214	MeCN	75	75.3	6.2	10.25	$C_{26}H_{26}FN_3O$	75.15	6.30	10.11	415	4.55	

* The $J_{4,5}$ was calculated in C_4D_4 solution

TABLE 3

N-Ethylidene-benzamidines

Product (6)	R^1	R^2	R^6	R^4	R^4_2N •	M.p. (°C)	Cryst. solvent	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N	M^+ (*m/e*)
a	Ph	Ph	Ph	Ph	M	171	EtOH	20	81.0	6.2	8.95	$C_{31}H_{29}N_3O$	81.01	6.36	9.14	459
b	Ph	Me	4-BrC_4H_4	Ph	M	111	EtOH	15	64.3	5.5	8.95	$C_{26}H_{26}BrN_3O$	65.54	5.50	8.82	475/477
c	4-BrC_6H_4	Me	Ph	Ph	M	145	Propan-2-ol	10	65.4	5.65	9.0	$C_{26}H_{26}BrN_3O$	65.54	5.50	8.82	475/477
d	Me	Me	Ph	Ph	M	88	Light Petroleum	80	75.05	7.55	12.55	$C_{21}H_{25}N_3O$	75.19	7.51	12.53	335
e	Me	Me	4-FC_6H_4	Ph	M	118	n-Hexane	85	71.05	6.95	11.7	$C_{21}H_{24}FN_3O$	71.36	6.84	11.89	353
f	Me	Me	4-MeC_6H_4	Ph	P	68	n-Hexane	80	79.2	8.6	12.3	$C_{23}H_{29}N_3$	79.49	8.41	12.09	347
g	Me	Me	4-MeC_6H_4	Ph	Py	Oil		75	78.5	8.45	12.15	$C_{22}H_{27}N_3$	79.24	8.16	12.60	333
h	—$[CH_2]_5$—		4-MeC_6H_4	Ph	M	96	n-Hexane	80	77.15	8.0	10.8	$C_{25}H_{31}N_3O$	77.08	8.02	10.79	389

• M = morpholino, P = piperidino, Py = pyrrolidino

solution of 1-morpholino-2-phenylpropene (2.0 g, 0.01 mol) in methanol (50 ml), the *N*-chloroamidine (2e) (2.5 g, 0.01 mol) was added. The reaction mixture was heated under reflux for a few minutes after which the solvent was evaporated under reduced pressure at 20—25 °C. The oily residue when worked up with a mixture of benzene–isopropylether (1 : 1) afforded a white solid (m.p. 238 °C, 2.4 g) of *N*-(4-fluorophenyl)benzamidine hydrochloride. This product was filtered off and the mother liquors were freed from the solvent under reduced pressure at room temperature. The oily residue of crude compound (12) was purified by distillation at 0.3 Torr (2 g, 75%), b.p. 130—135 °C), *m/e* 265 (M^+, 0.05%), 190 [$PhC(Me)\overset{+}{N}(CH_2)_2O(CH_2)_2$, 100%], 75 ($CH_3\overset{+}{O}=CH-O-CH_3$, 3%); δ_H ($CDCl_3$) 1.38 (3 H, s, CH_3), 2.53 (4 H, m, CH_2NCH_2), 3.12 and 3.38 (6 H, 2 s, OCH_3), 3.71 (4 H, t, CH_2OCH_2), 4.23 (1 H, s, CH), and 7.0—7.60 (5 H, m, Ph) (Found: C, 67.95; H, 8.7; N, 5.6. $C_{15}H_{23}NO_3$ requires C, 67.92; H, 8.67; N, 5.28).

^{1}H *N.m.r. Monitoring of the Reaction of* N-*Chloroamidine* (2e) *and* 1-*Morpholino-2-phenylpropene*.—A solution of (2e) (0.24 g, 0.001 mol), 1-morpholino-2-phenylpropene (0.20 g, 0.001 mol), and dry pyridine (0.088 g, 0.001 1 mol) in $CDCl_3$ (3.5 ml) was prepared and the ^{1}H n.m.r. spectrum immediately recorded (probe temperature, 37 °C). After 15 min the enamine signals had completely disappeared and the imidazoline ones were barely visible. The main signals detectable in this stage {δ_H 1.58 (3 H, s, CH_3), 2.3 [4 H, t, $N(CH_2)_2$], 3.59 [4 H, t, $O(CH_2)_2$], and 6.5—7.7 (14 H, m, aromatics} do not disagree with the proposed intermediate (10).

TABLE 4

N-Chloroamidines

Product (2)	R^5	R^6	M.p. (°C)	νNH (cm^{-1})	Cryst. solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
a	Ph	Ph	128 *	3 320	PhH	67.6	4.7	12.15	$C_{13}H_{11}ClN_2$	67.67	4.80	12.14
b	Ph	4-$NO_2C_6H_4$	128.5	3 350	EtOH	56.35	3.6	15.05	$C_{13}H_{10}ClN_3O_2$	56.63	3.65	15.24
c	Ph	4-BrC_6H_4	111	3 300	$Pr^i{}_2O$	50.45	3.25	9.05	$C_{13}H_{10}BrClN_2$	50.70	3.15	9.07
d	Ph	4-$MeOC_6H_4$	oil	3 350	—				$C_{14}H_{13}ClN_2O$			
e	Ph	4-FC_6H_4	68	3 300	$Pr^i{}_2O$	62.4	4.05	11.45	$C_{13}H_{10}ClFN_2$	62.78	4.05	11.26
f	Ph	4-MeC_6H_4	78	3 300	$Pr^i{}_2O$	68.85	5.3	11.35	$C_{14}H_{13}ClN_2$	68.70	5.35	11.44
g	Ph	$PhCH_2$	72	3 360	$Pr^i{}_2O$	68.6	5.5	11.6	$C_{14}H_{13}ClN_2$	68.70	5.35	11.44
h	4-BrC_6H_4	Ph	93	3 360	Cyclohexane	50.7	3.25	9.2	$C_{13}H_{10}BrClN_2$	50.42	3.25	9.04
i	Me	Ph	88	3 200	Light petroleum	56.5	5.65	16.4	$C_8H_9ClN_2$	56.97	5.37	16.61

* M.p. 130—131 °C, V. J. Grenda, R. E. Jones, G. Gal, and M. Sletzinger, *J. Org. Chem.*, 1965, **30**, 259.

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