Oxidative rearrangement and cyclisation of *N*-substituted amidines using iodine(III) reagents and the influence of leaving group on mode of reaction

Christopher A. Ramsden* and Helen L. Rose

Department of Chemistry, Keele University, Keele, Staffordshire, UK ST5 5BG

The products of reaction of *N*-substituted amidines 5 with hypervalent iodine reagents such as (diacetoxyiodo)benzene (DAIB), bis(trifluoroacetoxy)iodobenzene (BFIB) and [methoxy(tosyloxy)-iodo]benzene (MTIB) are determined by the reagent, the amidine substituents and the reaction temperature. *C*-Alkyl-*N*-arylamidines 5a–d cyclise in high yield giving benzimidazoles 6 but *C*,*N*-dialkyl- and *C*,*N*-diaryl-amidines 5e–l rearrange to give products derived from an intermediate carbodiimide. Use of N^2-phenylfuran-2-carboximidamide 5j leads to *N*-(2-furyl)acetamide 15 in good yield, illustrating a convenient route to stable derivatives of highly unstable 2-aminofuran. The rearrangement of *C*,*N*-diarylamidines on reaction with DAIB contrasts with the observed formation of benzimidazole when the same precursors are treated with lead tetraacetate (LTA). Evidence is presented to support the view that the mode of reaction is determined by the nature of the leaving group in an imide intermediate 19: very good leaving groups [*e.g.* PhI, N_2, AgCl and $PhSO_2O^-$ (aq.)] appear to favour rearrangement whereas poorer leaving groups [*e.g.* Cl^-, Me_2S, Me_3N and $PhSO_2O^-$ (non-aq.)] favour cyclo-α-elimination.

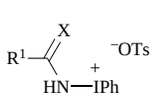
Introduction

We have a long-standing interest in the bonding and reactivity of molecules that can only be represented by dipolar or hypervalent structures. These interests have included the chemistry of mesoionic compounds[1] and heterocyclic mesomeric betaines.[2] Recently we have reviewed the relationship of these heterocycles to other 'non-classical' molecules associated with three-centre, four-electron [3*c*-4*e*] bonds and have emphasised common modes of reaction, such as *syn*-addition and ligand coupling, that arise from similarities in their electronic structure.[3] The association of all these molecules with a highest occupied molecular orbital (HOMO) that has the nodal properties of a non-bonding molecular orbital (NBMO) is of particular interest. These structural relationships have directed our attention to the investigation of novel reactions of hypervalent compounds of tellurium(IV), iodine(III)[4,5] and xenon(II)[6,7] and the application of this methodology to synthetic problems of biological interest. A useful property of these reagents, such as (diacetoxyiodo)benzene (DAIB) and xenon difluoride, is their ability to react first as an electrophile and then to be transformed into an exceptionally good leaving group (*i.e.* PhI or Xe). This particular aspect led to our recent description of two novel and closely related polar rearrangements of amidines[4] and trimethylsilyl esters[7] using DAIB and XeF_2 respectively.

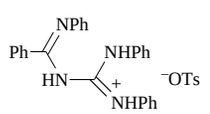
Amidines are potentially useful precursors of a variety of molecules of biological interest including nitrogen heterocycles. Our interest in biologically active imidazolines[8] and imidazoles[8,9] prompted us to investigate the reactions of N^2-substituted amidines with hypervalent iodine(III) reagents and we now wish to describe the results of this systematic study.

Results and discussion

Lazbin and Koser[10] have described the isolation of *N*-phenyliodoniocarboxamide toluene-*p*-sulfonates (tosylates) **1** by reaction of the corresponding carboxamide with [methoxy-(tosyloxy)iodo]benzene (MTIB) in acetonitrile at room temperature. Our initial interest in amidines was prompted by the possibility that similar derivatives of N^2-substituted amidines (*i.e.* **2**) could be useful intermediates for coupling amidines to alkenes or alkynes. However, all our attempts to isolate compounds of the type **2** were unsuccessful. When N^2-phenylbenzamidine **5i** in acetonitrile was treated with one equivalent of MTIB at room temperature or below a mixture of products was rapidly formed. The main products were identified as iodobenzene, N^2-phenylbenzamidin-N^2-ium tosylate, diphenylcarbodiimide trimer and N^1,N^2-diphenyl[phenyl(phenylimino)-methylamino]formamidin-N^2-ium tosylate **3**. A cleaner reaction was achieved when one equivalent of MTIB was added to three equivalents of the amidine at reflux temperature with subsequent addition of one equivalent of toluene-*p*-sulfonic acid to convert all amidine derivatives to their salts. These conditions gave N^2-phenylbenzamidin-N^2-ium tosylate (43%) and the salt **3** (29%). The latter product is clearly formed by reaction of the amidine precursor with diphenylcarbodiimide which must be generated *in situ* by oxidative rearrangement of the amidine precursor. The structure of this rearranged product **3** was fully supported by its spectroscopic properties which were identical with those of an authentic sample prepared by reaction of diphenylcarbodiimide with N^2-phenylbenzamidine **5i**. As far as we are aware, direct C to N rearrangements of primary amidines **5** have not previously been reported.



1; X = O
2; X = NR^2



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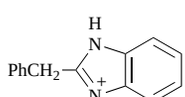

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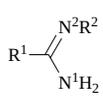
In contrast, when (N^2-phenyl)phenylacetimidamide **5a** was treated with MTIB under similar conditions no rearranged products were formed and the main product was 2-benzylbenzimidazol-1-ium tosylate **4** (42%) together with (N^2-phenyl)-phenylacetamidin-N^2-ium tosylate (**5a**·TsOH) (34%). From our initial studies it became clear that the course of these reactions is determined by the amidine substituents and the type of iodine(III) reagent. We therefore carried out an investigation of a range of amidine derivatives and the

Table 1 Reaction of *N*-substituted amidines **5** with diacetoxyiodobenzene (DAIB)

				Product yields (%)			
Amidine	R^1	R^2	*T*/°C	**6**	**11**	**12**	**13**
5a	$PhCH_2$	Ph	110	82	—	—	—
5b	Cyclohexyl	Ph	110	95	—	—	—
5c	Et	Ph	110	72	—	—	—
5d	$C_{10}H_{11}O$ [a]	Ph	110	67	—	—	—
5e	$PhCH_2$	Cyclohexyl	110	—	17	77	—
			80	—	—	83	—
5f	Cyclohexyl	$PhCH_2$	110	—	27	56	—
5g	Cyclohexyl	Cyclohexyl	110	—	21	28	—
			80	—	—	68	—
5h	$PhCH_2$	$4\text{-}MeC_6H_4CH_2$	110	—	—	23	—
5i	Ph	Ph	110	—	—	—	99
			80	9	75	—	—
			50	16	65	—	—
			25 [b]	—	—	26	—
5j	2-Furyl	Ph	110	—	—	—	99
			80	—	67	—	—
5k	Ph	$4\text{-}NO_2C_6H_4$	110	—	17	—	56 [c]
5l	$4\text{-}MeOC_6H_4$	Ph	110	—	—	—	90
5m	Ph	Cyclohexyl	110	—	—	—	96

[a] 2,3-Dihydro-2-ethylbenzo[*b*]furan-2-yl. [b] Diphenylcarbodiimide trimer (30%) (mp 163–166 °C) was also formed under these conditions. [c] Product had structure **14**.



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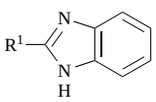

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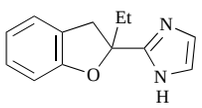

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In formulae **5, 8–14**;

a $R^1 = PhCH_2$, R^2 = Ph;
b R^1 = cyclohexyl, R^2 = Ph;
c R^1 = Et, R^2 = Ph;
d R^1 = 2,3-dihydro-2-ethylbenzo[*b*]furan-2-yl, R^2 = Ph
e $R^1 = PhCH_2$, R^2 = cyclohexyl;
f R^1 = cyclohexyl, $R^2 = PhCH_2$;
g $R^1 = R^2$ = cyclohexyl;
h $R^1 = PhCH_2$, $R^2 = 4\text{-}MeC_6H_4CH_2$;
i $R^1 = R^2$ = Ph;
j R^1 = 2-furyl, R^2 = Ph;
k R^1 =Ph, $R^2 = 4\text{-}NO_2C_6H_4$;
l $R^1 = 4\text{-}MeOC_6H_4$, R^2 =Ph;
m R^1 = Ph, R^2 = cyclohexyl;
n R^1 = Ph, R^2 = 2-furyl;
o $R^1 = 4\text{-}NO_2C_6H_4$, R^2 = Ph.

results, which are described below and summarised in Table 1, are subdivided according to whether the substituents are alkyl or aryl.

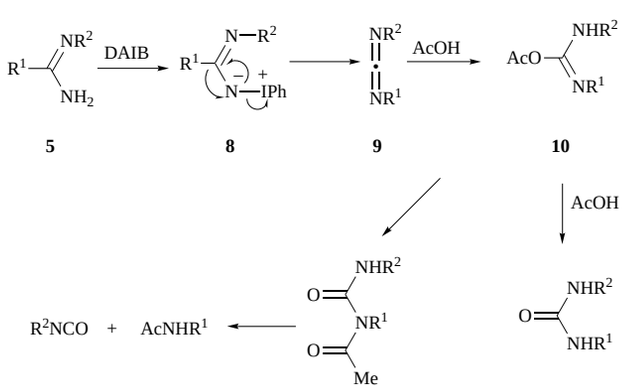
The amidines used in this study (**5a**–**k**) were synthesised in good yield using three methods. In most cases the corresponding nitrile was reacted with a primary amine using either sodamide (Method A)[11] or aluminium chloride (Method B)[12] as a catalyst. In one case (**5k**) the corresponding secondary amide was converted to the imidoyl chloride which was then treated with ethanolic ammonia (Method C).[13] All amidines were purified by recrystallisation and were fully characterised using spectroscopic and microanalytical methods.

C-Alkyl-*N*-arylamidines 5a–d

Reaction of (N^2-phenyl)phenylacetimidamide **5a** with DAIB in toluene at reflux temperature gave 2-benzylbenzimidazole **6** (R = $PhCH_2$) in good yield (82%). Apart from iodobenzene, no other products were identified. In a similar manner, the ethyl and cyclohexyl derivatives (**6**; R = Et, cyclohexyl) were also prepared in high yield. For this transformation (**5** ⟶ **6**) the use of DAIB is cleaner and higher yielding than MTIB and also avoids the formation of the benzimidazolium salt (*cf*. **4**). Other oxidising agents, including manganese dioxide[14] and lead tetraacetate (LTA),[15] have been used to transform *N*-arylamidines to benzimidazoles. However, DAIB appears to be particularly convenient, and also has distinct advantages over LTA.[5] We have applied this procedure to the preparation of the benzimidazole analogue of the islet imidazoline receptor antagonist KU14R **7**:[8] the desired benzimidazole **6** (R = 2,3-dihydro-2-ethylbenzo[*b*]furan-2-yl) was obtained from the amidine precursor **5d** in 67% yield.

C,*N*-Dialkylamidines 5e–h

If a nitrene intermediate were involved in the formation of the benzimidazoles **6** then in principle it would be possible for this intermediate to insert into a C–H bond of an *N*-alkylamidine substituent to form an imidazoline derivative. This would be an attractive route to imidazolines of biological interest. To explore this possibility (N^2-cyclohexyl)phenylacetimidamide **5e** was treated with DAIB. In contrast to the previously observed cyclisation of the N^2-phenyl analogue **5a**, a rearrangement occurred giving *N*-benzyl-*N′*-cyclohexylurea **12e** as the major product (77%). At 110 °C a small amount of the *N*-acetylurea **11e** (17%) was also formed but at 80 °C the urea **12e** was the only product (83%). A mechanism for the formation of these products *via* a carbodiimide intermediate **9** is shown in Scheme 1.



5 **8** **9** **10** **11** **12**

Scheme 1

We propose the initial formation of an ylide intermediate **8** that undergoes a C to N rearrangement, analogous to the Hofmann rearrangement, to give the carbodiimide **9**. This intermediate **9** then reacts with acetic acid, formed from the DAIB, to give the *O*-acetylurea **10**. Protonation occurs on the most basic nitrogen atom,[16] which in the case of the carbodiimide **9e** is *N*-cyclohexyl. The behaviour of *O*-acetylureas **10** has been studied by a number of workers[17] and for *N*,*N*′-dialkyl derivatives reaction with a second molecule of acetic acid commonly occurs leading to formation of *N*,*N*′-dialkylureas **12** together with acetic anhydride. Alternatively, the acetyl group can migrate to the less basic nitrogen atom to give the *N*-acetylurea **11** and this pathway accounts for the small amount of compound **11e** at 110 °C. The constitution of this product **11e** was established by examination of its mass spectrum which showed a weak molecular ion at *m*/*z* 274 (5%) with the base peak at *m*/*z* 149 ($PhCH_2NHCOMe^{\bullet+}$) corresponding to loss of cyclohexyl isocyanate by McLafferty rearrangement of the molecular ion. When the isomeric amidine **5f** was treated with DAIB at 110 °C the urea **12f** (≡**12e**) (56%) was accompanied by the same *N*-acetylurea isomer **11e** (27%). This result suggests the intermediacy of the free carbodiimide which subsequently protonates on the most basic nitrogen (*N*-cyclohexyl).

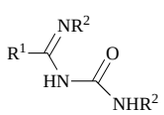
At 110 °C the dicyclohexylamidine **5g** gave the urea **12g** (28%) and the *N*-acetylurea **11g** (21%) together with *N*-cyclohexylacetamide (32%), which is formed by thermal elimination of cyclohexyl isocyanate from compound **11g** (Scheme 1). This transformation (**11** ⟶ $AcNHR^1 + R^2NCO$) can be rationalised in terms of a concerted intramolecular proton transfer involving a six-membered transition state. At 80 °C the amidine **5g** gave only the urea **12g**; formation of the acetyl derivatives (*e.g.* **11e**,**g**) is clearly favoured by higher temperatures. At 50 °C and below no reaction occurred. Even at 110 °C, the amidine **5h** gave only the urea **12h** (73%).

It is interesting to note that when the reaction of the amidine **5g** with bis(trifluoroacetoxy)iodobenzene (BFIB) was investigated at 100, 80 and 25 °C, under identical conditions to those using DAIB, only the trifluoroacetate salt of the amidine **5g** (60–70%) was isolated together with unreacted BFIB. This difference in behaviour must be related to the difference in the pK_a values of TFA and acetic acid.

C,*N*-Diarylamidines 5i–l

It was of interest to determine whether diarylamidines **5** (R^1, R^2 = Ar) undergo rearrangement to carbodiimides (**5** ⟶ **9**) or cyclisation to benzimidazoles (**5** ⟶ **6**). The latter reaction is known to occur using LTA.[15] We now report a significant difference between the reactions of these amidines with DAIB and with LTA under the same conditions. Four diarylamidines **5i–l** were investigated and were selected to give significant variation of the electronic character of the aryl substituents.

When N^2-phenylbenzimidamide **5i** was reacted with DAIB in toluene solution at reflux temperature the isolated products were N^1-(*N*-phenylcarbamoyl)-N^2-phenylbenzimidamide **13i**



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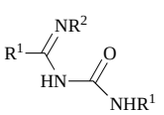

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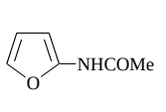

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(99%) and acetanilide (80%). However, when the reaction was carried out at 80 °C the product was *N*-acetyl-*N*,*N*′-diphenylurea **11i** (75%) together with a low yield of 2-phenylbenzimidazole **6** (R = Ph) (9%). These results are significantly different from those reported[15] for the reaction of N^2-phenylbenzimidamide **5i** with LTA which under identical conditions we have confirmed gives exclusively 2-phenylbenzimidazole **6** (R = Ph) in yields of 86% (110 °C) and 70% (80 °C). The formation of the DAIB products **11i** and **13i** can be rationalised according to the pathway shown in Scheme 1. At 80 °C diphenylcarbodiimide **9i**, formed by rearrangement, gives the *N*-acetylurea **11i** which is isolated: at 110 °C this product **11i** undergoes thermal elimination of phenyl isocyanate which reacts with the precursor amidine **5i** to give the observed product **13i**. In contrast to *N*,*N*′-dialkylcarbodiimides, it is known[17] that *N*,*N*′-diarylcarbodiimides react with acetic acid *via* the *O*-acyl derivatives **10** to give the rearranged *N*-acylureas **11** ($R^1 = R^2$ = Ar) rather than the ureas **12** ($R^1 = R^2$ = Ar) (Scheme 1). The yield of 2-phenylbenzimidazole **6** (R = Ph) increased slightly (16%) when the reaction was carried out at 50 °C but the major product was still the *N*-acylurea **11i** (65%). When the reaction was performed at 25 °C the products were diphenylcarbodiimide trimer (30%) and diphenylurea (26%), providing direct evidence that a carbodiimide is a true intermediate in these reactions.

The formation of 2-phenylbenzimidazole **6** (R = Ph) in modestly increasing yields as the temperature is lowered [*i.e.* 110 °C (0%); 80 °C (9%) and 50 °C (16%)] merits some comment. The free energy of activation for the cyclo-α-elimination reaction (**8i** ⟶ **6**) is almost certainly associated with a negative entropy of activation ($\Delta S^{\ddagger}$ negative) due to ring formation whereas the rearrangement (**8i** ⟶ **9**) is not expected to have an unfavourable entropy component (*i.e.* $\Delta S^{\ddagger} \approx 0$). As a result the $-T\Delta S^{\ddagger}$ contribution to the activation energy for the cyclisation can be expected to be significant but to decrease with decreasing temperature. This is in agreement with the experimental observations.

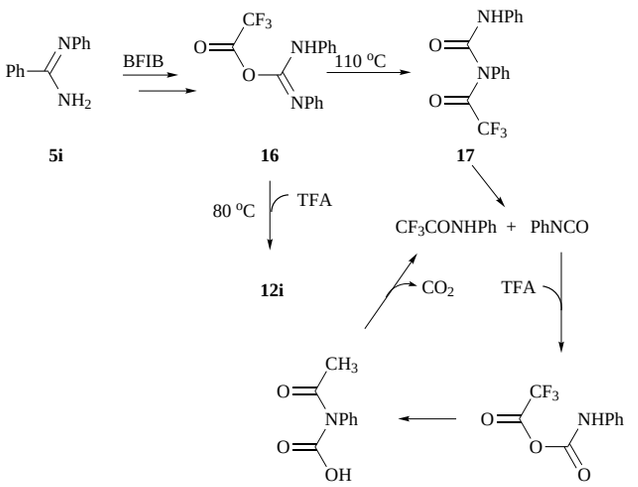
Similar results were obtained using N^2-phenylfuran-2-carboximidamide **5j**. Treatment with DAIB at 110 °C gave exclusively the *N*-phenylcarbamoyl derivative **13j** (99%) but at 80 °C the precursor *N*-acylurea **11j** was obtained (67%). The proposal that the *N*-acylureas **11** undergo thermal elimination of aryl isocyanate at 110 °C (Scheme 1) was confirmed by heating compound **11j** at 110 °C in toluene solution in the presence of one equivalent of aniline. Under these conditions the phenyl isocyanate was trapped as diphenylurea and *N*-(2-furyl)acetamide **15** (88%) was obtained. This approach therefore provides a simple route to 2-aminofuran derivatives, which are difficult to obtain by other methods due to the intrinsic instability of 2-aminofuran.[18,19] When compound **5j** was treated with LTA the product was 2-(2-furyl)benzimidazole **6** (R = 2-furyl) (65%), confirming the fundamental difference in the mode of reaction of LTA from that of DAIB.

An interesting facet of the reaction of the 2-furyl derivative **5j** at 80 °C is that only the *N*-acylurea **11j** is formed and there is none of the regioisomer **11n**: the acyl group migrates exclusively to the *N*-furyl position. We interpret this result in terms of initial protonation of the most basic nitrogen atom of the intermediate carbodiimide,[16] which in this case is *N*-Ph. Formation of the *O*-acylurea **10j** then occurs followed by migration to the less basic, unprotonated nitrogen atom. These conclusions are supported by the results obtained using the N^2-(*p*-nitrophenyl) amidine derivative **5k** which at 110 °C gave the *N*-phenylcarbamoyl derivative **14k** (56%) and *p*-nitroacetanilide (17%) together with some of the precursor *N*-acylurea **11o** (17%). Again the least basic nitrogen atom [*N*-(*p*-$NO_2C_6H_5$)] had been acylated. This result confirms that the position of the nitrogen atom in the precursor amidine does not determine the position of *N*-acylation of the ureas **11** and provides further evidence of the formation of a free carbodiimide intermediate **9**. This rationalisation is also consistent with the regiospecificity described above for the dialkylamidines **5e** and **5f** which give the same regioisomer **11e**.

At first sight the results using N^2-phenyl-4-methoxybenzimidamide **5l** appear to contradict our mechanistic conclusions. Thus, reaction with DAIB gives the *N*-phenylcarbamoyl derivative **13l** (90%) and *p*-methoxyacetanilide (85%). These products require the intermediate formation of the *N*-acylurea

11l in which the most basic nitrogen atom [*N*-(*p*-$MeOC_6H_5$)] is acylated. However, we believe that in the non-polar, hydrophobic environment of the toluene solution the acetic acid (two equivalents) liberated in the reaction will result in protonation of the methoxy substituent of the carbodiimide. This will render the neighbouring nitrogen atom the least basic under the conditions of the reaction and acylation therefore occurs on *N*-(4-$MeOC_6H_4$).

Some interesting differences were observed when bis(trifluoroacetoxy)iodobenzene (BFIB) was reacted with the diphenyl derivative **5i**. At 110 °C the products were the trifluoroacetate salts of 2-phenylbenzimidazole **6** (R = Ph) (28%) and starting material **5i** (33%) together with *N*-phenyltrifluoroacetamide (28%). Lowering the temperature to 80 °C also gave the same salts in 22% and 53% yield respectively but *N*,*N*-diphenylurea **12i** (17%) was obtained instead of *N*-phenyltrifluoroacetamide. It is not clear why more of the cyclised product **6** (R = Ph) is formed using BFIB but the observation of the urea **12i** among the products indicates that rearrangement also occurs. We tentatively suggest that at 80 °C the *O*-trifluoroacetylurea **16** gives the urea **12i** and trifluoroacetic anhydride (*cf*. **10** ⟶ **12**; Scheme 1) whereas at 110 °C rearrangement to the *N*-trifluoroacetylurea **17** leads to trifluoroacetamide and phenyl isocyanate (Scheme 2).[20] Reaction of phenyl isocyanate with



Scheme 2

TFA may then lead to more trifluoroacetamide *via* O to N trifluoroacyl transfer and elimination of carbon dioxide.[20,21]

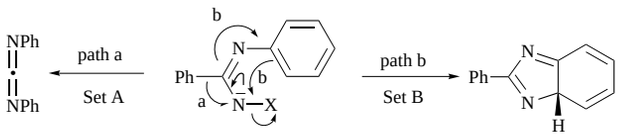
C-Aryl-*N*-alkylamidines 5m

We have investigated only one *C*-aryl-*N*-alkylamidine **5m** and the observed mode of reaction is consistent with the results and conclusions for the related systems. Thus, compound **5m** gave the *N*-cyclohexylcarbamoyl derivative **13m** (96%) and acetanilide (99%). In accord with expectation the acetyl group migrates to the least basic nitrogen (*N*-Ph) and cyclohexyl isocyanate is generated as a reaction intermediate.

Influence of leaving group on mode of reaction

Although the reactions of *N*-arylamidines with iodine(III) reagents that are described in the preceding sections are new, we recognise that they belong to a general class of reactions of *N*-arylamidine derivatives that are mediated by species of the general type **19**, where X is a leaving group. Since the reactions of these species (*e.g.* **19**) have not previously been discussed collectively it is instructive to consider how the nature of the leaving group X influences the mode of reaction. Viewed in this general context our results are very satisfactorily rationalised in terms of the intermediate species **8** (Scheme 1) in which the leaving group (X) is iodobenzene (PhI). The following discussion refers specifically to the diphenyl species **19** for which a comprehensive set of experimental data is available in the literature.

Two modes of reaction can be recognised for the general species **19**. Loss of the leaving group X and rearrangement (path a, Scheme 3) leads to a carbodiimide **18** which may



18 **19** **20**

Leaving groups: Set A; X = PhI^+, N_2^+, $AgCl^+$, $PhSO_2O$ (aq.)
Set B; X = Cl, Me_2S^+, Me_3N^+, $PhSO_2O$ (non-aq.)
Set C; X = Ph_3P^+

Scheme 3

undergo further reaction (*e.g.* Scheme 1). Alternatively, a cyclo-α-elimination reaction can occur (path b, Scheme 3) giving the bicyclic product **20** which rearranges to the observed benzimidazole **6** (R = Ph). Usually only one mode of reaction (path a or b) is observed and the preferred reaction appears to be dependent on the nature of the leaving group X. As discussed above, lower temperatures will also tend to make path b become more favourable.

The leaving groups X that have been studied can be divided into three sets (Sets A–C, Scheme 3) each of which shows different behaviour. Set A includes the functional groups PhI^+, N_2^+,[22] $AgCl^+$[23] and $PhSO_2O$ (in aqueous media).[24] All these functions are exceptionally good leaving groups and reaction appears to be dominated by N–X bond cleavage leading to diphenylcarbodiimide **18** (Schemes 1 and 3). Analogy can be made with an S_N1 reaction but we do not wish to imply that a nitrene intermediate is necessarily formed since migration of the *C*-substituent probably commences before cleavage of the N–X bond is complete. The process is probably concerted but facilitated by the weakness of the N–X bond and the stability of the products [*i.e.* PhI, N_2, AgCl or $PhSO_2O^-$ (aq.)].

In contrast, when X is not such a good leaving group such as those in Set B, the benzimidazole formed *via* cyclo-α-elimination (path b, Scheme 3) is the observed product. The leaving groups include Cl^-,[25] Me_2S,[26] Me_3N[27] and $PhSO_2O^-$ (in non-aqueous media).[28] For this type of leaving group X the results are consistent with the assumption that reaction is initiated by nucleophilic attack on nitrogen and that N–X bond breaking and C–N bond formation occur simultaneously. The process in this case is analogous to an S_N2 reaction.

Using these two sets of leaving groups as a database it is interesting to speculate on the difference in behaviour that we have seen between DAIB and LTA. The mechanism of reaction of LTA is not clear but for reaction with N^2-phenylbenzimidamide **5i** it is reasonable to propose the intermediate **19** [X = $Pb(OAc)_3$ or $Pb^+(OAc)_2$].[29] Since the product is exclusively 2-phenylbenzimidazole **6** (R = Ph) the lead substituent is appropriately classified with the Set B leaving groups (Scheme 3). The difference in behaviour between LTA and DAIB can therefore be assigned to the difference in the strengths of the N–I and N–Pb bonds. There are many examples of LTA and DAIB giving the same products[5] and in these cases the relative stabilities of the relevant iodine and lead bonds do not influence the mode of reaction. Where differences are observed[30] then the relative strengths of these bonds in key intermediates may well account for alternative modes of reaction.

For the specific case of X = Ph_3P^+ (Set C, Scheme 3) a different mode of reaction occurs and the products are benzonitrile and tetraphenylphosphimide ($PhN^-–P^+Ph_3$).[31] Here, as in the case of the Wittig reaction, the phosphorus atom participates in a four-membered cyclisation leading to the observed products.

Experimental

Melting points were determined using a Reichert Kofler Block apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 881 spectrophotometer with only major absorbances being quoted. Unless otherwise stated IR spectra were measured as KBr discs. ^{1}H NMR Spectra were recorded at ambient temperatures using a JEOL GSX270 FT-NMR spectrometer with tetramethylsilane (TMS) as an internal reference, and were run in deuterated chloroform solution unless otherwise stated. Chemical shifts are quoted in parts per million and the following abbreviations are used: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. Coupling constants (*J*) are given in Hz. Elemental analyses were determined using a Perkin-Elmer 240 CHN Elemental Analyser. Low resolution mass spectra were recorded on an AEI MS12 Mass Spectrometer at 70 eV electron impact ionisation. Separations by column chromatography were carried out using aluminium oxide (150 mesh, Aldrich) deactivated with water to Brockmann grade IV unless otherwise stated. Flash chromatography was performed using silica gel (Janssen Chimica) 0.035–0.07 mm. Preparative radial (chromatotron) chromatography was carried out on a Harrison Research Ltd. Chromatotron 7924 using a 2 mm plate with silica gel 60 PF_{254} containing gypsum (Merck). All solvents were pre-distilled and dried appropriately prior to use. Concentration and evaporation refer to the removal of volatile materials under reduced pressure on a Büchi Rotovapor. Substances stated to be identical were so with respect to mps, mixed mps and IR spectra.

Preparation of amidines

Method A. (N^2-Phenyl)phenylacetimidamide 5a. To a mixture of sodamide (4.3 g, 0.11 mol) and aniline (9 cm^3, 0.1 mol) stirring in dry toluene (100 cm^3) at 40 °C was added slowly benzyl cyanide (11.5 cm^3 0.1 mol). Formation of a beige solid was observed. The mixture was heated under reflux (24 h) and to the cooled solution was added absolute ethanol (25 cm^3) and lactic acid (75% solution, 90 cm^3). Aqueous ammonia (35%, ~80 cm^3) was added and the brown crystalline product was collected, recrystallised from acetonitrile and identified as compound **5a** (17.2 g, 82%), buff crystals, mp 137–141 °C (lit.,[32] 140–141 °C) (Found: C, 80.25; H, 6.7; N, 13.2. Calc. for $C_{14}H_{14}N_2$: C, 80.0; H, 6.7; N, 13.3%); ν_{max}/cm^{-1} 3417, 3102, 2899, 1639, 1586, 1479, 1289; δ_H($CDCl_3$) 3.67 (s, CH_2), 4.4 (br s, 2H), 6.9–7.05 (m, 3H), 7.25–7.36 (m, 7H); *m/z* 210 ($M^{\bullet+}$).

In a similar manner the following amidine was prepared from 2-furonitrile.

N^2-*Phenylfuran*-2-*carboximidamide* **5j** (72%), buff crystals, mp 105–106 °C (Found: C, 71.1; H, 5.3; N, 15.1. $C_{11}H_{10}N_2O$ requires C, 70.95; H, 5.4; N, 15.0%); ν_{max}/cm^{-1} 3458, 3329, 3291, 3109, 3070, 1625, 1561, 1478, 1404, 1026; δ_H($CDCl_3$) 4.99 (br s, 2H), 6.49–6.52 (m, 1H), 6.97–7.47 (m, 7H); *m/z* 186 ($M^{\bullet+}$).

Method B. N^2-Phenylcyclohexanecarboximidamide 5b. To a mixture of cyclohexyl cyanide (10.9 g, 0.1 mol) and aniline (9.3 g, 0.1 mol) was added powdered aluminium chloride (13.35 g, 0.1 mol) in portions with constant swirling. A vigorous exothermic reaction occurred and the mixture became thick and turned brown. The solution was added to hot water (~100 cm^3) and a buff solid separated. The solution was basified (30% aqueous NaOH) to pH 14, extracted with chloroform, dried (Na_2SO_4) and evaporated. The resulting solid was washed with a small volume of cold diethyl ether, air dried to constant mass, recrystallised from acetonitrile and identified as *compound* **5b** (19.76 g, 98%), colourless plates, mp 129–130 °C (Found: C, 77.2; H, 9.1; N, 14.0. $C_{13}H_{18}N_2$ requires C, 77.2; H, 9.0; N, 13.85%); ν_{max}/cm^{-1} 3452, 3296, 3116, 2930, 2852, 1638, 1586, 1482, 1442, 1410, 1340, 1286, 1252, 1220; δ_H($CDCl_3$) 1.22–2.04 (m, 10H), 2.19–2.27 (m, 1H), 4.34 (br s, 2NH), 6.85–6.88 (m, 2H), 6.96–7.02 (m, 1H), 7.25–7.31 (m, 2H); *m/z* 202 ($M^{\bullet+}$).

In a similar manner the following amidines were prepared from the appropriate alkyl cyanide.

N^2-*Phenylpropionimidamide* **5c** (90%), pale yellow crystals, mp 70–71.5 °C (Found: C, 73.1; H, 8.2; N, 18.8. $C_9H_{12}N_2$ requires C, 72.9; H, 8.2; N, 18.9%); ν_{max}/cm^{-1} 3418, 3288, 3146, 2974, 1636, 1586, 1280, 1388, 1232, 1066; δ_H($CDCl_3$) 1.23 (t, *J* 7.32 , 3H), 2.29 (q, *J* 7.32, 2H), 4.49 (br s, 2H), 6.84–6.87 (m, 2H), 6.96–7.02 (m, 1H), 7.25–7.31 (m, 2H); *m/z* 148 ($M^{\bullet+}$).

N^2-*Phenyl*-2,3-*dihydro*-2-*ethylbenzo*[b]*furan*-2-*carboximidamide* **5d** (25%), colourless prisms, mp 71–72 °C (Found: C, 77.0; H, 7.0; N, 10.4. $C_{17}H_{18}N_2O$ requires C, 76.7; H, 6.8; N, 10.5%); ν_{max}/cm^{-1} 3460, 3261, 3134, 1636, 1581, 1480, 1459, 1385, 1241; δ_H($CDCl_3$) 1.09 (t, *J* 7.3, 3H), 2.07 (m, 1H), 2.23 (m, 1H), 3.30 (d, *J* 16, 1H), 3.88 (d, *J* 16, 1H), 5.05 (br s, 2H), 6.8–7.3 (m, 9H); *m/z* 266 ($M^{\bullet+}$).

N^2-*Benzylcyclohexanecarboximidamide* **5f** (81%), small colourless crystals, mp 113–114.5 °C (Found: C, 78.0; H, 9.55; N, 13.1. $C_{14}H_{20}N_2$ requires C, 77.7; H, 9.3; N, 12.95%); ν_{max}/cm^{-1} 3460, 3312, 3060, 2930, 2852, 1654, 1606, 1444, 1200, 1170; δ_H($CDCl_3$) 1.23–1.43 (m, 5H), 1.69–2.08 (m, 6H), 4.39 (s, 2H), 7.24–7.36 (m, 5H) (no NH); *m/z* 216 ($M^{\bullet+}$).

N^2-*Cyclohexylcyclohexanecarboximidamide* **5g** (72%), colourless crystals, mp 128–128.5 °C (Found: C, 75.0; H, 12.2; N, 13.4. $C_{13}H_{24}N_2$ requires C, 74.9; H, 11.6; N, 13.45%); ν_{max}/cm^{-1} 3240, 3080, 2928, 2848, 1594, 1448, 1340, 1168; δ_H($CDCl_3$) 1.02–1.48 (m, 10H), 1.58–2.01 (m, 11H), 3.58–3.70 (m, 1H), 4.10 (br s, 2H); *m/z* 208 ($M^{\bullet+}$).

N^2-(4-*Methylbenzyl*)*phenylacetimidamide* **5h** (72%), buff plates, mp 125–129.5 °C (Found: C, 80.6; H, 7.35; N, 11.9. $C_{16}H_{18}N_2$ requires C, 80.6; H, 7.6; N, 11.75%); ν_{max}/cm^{-1} 3194, 3024, 2926, 2846, 1604, 1390, 1162; δ_H($CDCl_3$) 2.32 (s, 3H), 3.58 (s, 2H), 4.36 (s, 2H), 4.7 (br s, 2H), 7.10–7.37 (m, 9H); *m/z* 238 ($M^{\bullet+}$).

N^2-*Phenyl*-4-*methoxybenzimidamide* **5l** (60%), colourless crystals, mp 150–150.5 °C (Found: C, 74.4; H, 6.4; N, 12.7. $C_{14}H_{14}N_2O$ requires C, 74.3; H, 6.2; N, 12.4%); ν_{max}/cm^{-1} 3448, 3306, 3146, 1632, 1608, 1586, 1560, 1382, 1254, 1192, 1022; δ_H($CDCl_3$) 3.83 (s, 3H), 4.79 (br s, 2H), 6.90–6.98 (m, 4H), 7.01–7.07 (m, 1H), 7.30–7.36 (m, 2H), 7.79–7.82 (m, 2H); *m/z* 226 ($M^{\bullet+}$).

Method C. N^2-(4-Nitrophenyl)benzimidamide 5k. *N*-(4-Nitrophenyl)benzimidoyl chloride[33] (13.0 g, 0.049 mol) was stirred in absolute ethanol (150 cm^3) at 0 °C and ammonia gas passed through the solution (3 h). Evaporation afforded a liquid which solidified upon refrigeration and after recrystallisation from chloroform was identified as *compound* **5k** (10.52 g, 87%), yellow crystals, mp 167–168.5 °C (Found: C, 64.8; H, 4.4; N, 17.5. $C_{13}H_{11}N_3O_2$ requires C, 64.7; H, 4.6; N, 17.4%); ν_{max}/cm^{-1} 3478, 3366, 3108, 2808, 1644, 1576, 1486, 1334, 1256, 1102; δ_H($CDCl_3$–[$^2H_6$]DMSO) 6.59 (br s, 2H), 7.10 (d, *J* 8.79, 2H), 8.21 (d, *J* 8.79, 2H), 7.42–7.54 (m, 3H), 7.84–7.87 (m, 2H); *m/z* 241 ($M^{\bullet+}$).

The following amidines were prepared according to literature procedures: N^2-cyclohexylbenzimidamide **5m**,[32] (N^2-cyclohexyl)phenylacetimidamide **5e**.[34] N^2-Phenylbenzimidamide **5i** was purchased from Maybridge Chemical Co. Ltd.

Reactions of amidines with methoxy(tosyloxy)iodobenzene (MTIB)

(N^2-Phenyl)phenylacetimidamide 5a. To a stirred solution of amidine **5a** (1.05 g, 5 mmol) in dry acetonitrile (30 cm^3) heated under reflux was added dropwise a solution of MTIB[35] (2.03 g, 5 mmol) in acetonitrile (30 cm^3). After refrigeration, a solid formed which was recrystallised from acetonitrile and identified as 2-*benzylbenzimidazol*-1-*ium toluene*-p-*sulfonate* **4** (0.8 g, 42%), colourless needles, mp 184.5–186.5 °C (Found: C, 66.2; H, 5.2; N, 7.45. $C_{21}H_{20}N_2SO_3$ requires C, 66.3; H, 5.3; N, 7.4%); ν_{max}/cm^{-1} 3062, 2926, 2750, 2638, 1242, 1150, 1112, 1030, 1008; δ_H([$^2H_6$]DMSO) 2.29 (s, 3H), 4.53 (s, 2H), 7.10–7.51 (m, 9H), 7.54 (dd, *J* 3.18 and 3.17, 2H), 7.79 (dd, *J* 3.18 and 3.17, 2H),

(no NH); *m/z* 208, 209 (benzimidazole $M^{\bullet+}$, M + 1), 172 ($TsOH^{\bullet+}$). Continued refrigeration of the mother liquor resulted in selective crystallisation of a second product that was recrystallised from acetonitrile and identified as (N^2-phenyl)-phenylacetamidin-N^2-ium toluene-*p*-sulfonate **5a**·TsOH (0.65 g, 34%), colourless needles, mp 133–135 °C identical with an authentic sample.

In a similar manner N^2-phenylbenzimidamide **5i** (0.59 g, 3 mmol) was reacted with MTIB (0.41 g, 1 mmol) at room temperature. Toluene-*p*-sulfonic acid monohydrate (0.19 g, 1 mmol) in acetonitrile (2 cm^3) was added to the reaction mixture which was then separated by column chromatography (silica gel, acetic acid as eluent) to give N^2,N^2-diphenyl[phenyl(phenylimino)methylamino]formamidin-N^2-ium toluene-*p*-sulfonate **3** (0.32 g, 29%), fine plates, mp 194–196 °C, identical to an authentic sample and *N*-phenylbenzamidin-N^2-ium toluene-*p*-sulfonate (0.47 g, 43%), mp 154–156 °C (Found: C, 65.5; H, 5.2; N, 7.4. Calc. for $C_{20}H_{20}N_2SO_3$: C, 65.2; H, 5.5; N, 7.6%); ν_{max}/cm^{-1} 3010, 1635, 1585, 1524, 1477, 1204, 1160, 1117, 1029, 1005; $\delta_H(CDCl_3)$ 2.33 (s, 3H), 7.1 (d, *J* 7.8, 2H), 7.6 (d, *J* 7.8, 2H), 7.45–7.95 (m, 10H), 9.25 (br s, 3H); *m/z* 196 (amidine $M^{\bullet+}$).

Reactions of amidines with diacetoxyiodobenzene (DAIB)

(i) At 110 °C. (N^2-Phenyl)phenylacetimidamide 5a. To a solution of DAIB (0.644 g, 2 mmol) in distilled toluene (10 cm^3) heated under reflux was added dropwise a solution of amidine **5a** (0.42 g, 2 mmol) in toluene (10 cm^3). After evaporation the residue was purified by flash chromatography on silica (chloroform; chloroform–10% methanol as eluent). In addition to iodobenzene, one major product was obtained. The material was recrystallised from acetonitrile and identified as 2-benzylbenzimidazole **6** (R = $PhCH_2$) (0.34 g, 82%), colourless needles, mp 187.5–189 °C (lit.,[36] 188–189 °C) (Found: C, 80.8; H, 5.6; N, 13.3. Calc. for $C_{14}H_{12}N_2$: C, 80.7; H, 5.8; N, 13.45%); ν_{max}/cm^{-1} 3006, 2838, 2736, 2684, 1530, 1424, 1268, 1020; $\delta_H([^2H_6]DMSO)$ 4.17 (s, CH_2), 7.10–7.52 (m, 9 ArH), 12.29 (br s, 1NH); *m/z* 208 ($M^{\bullet+}$).

In a similar manner the following transformations were achieved.

(a) N^2-Phenylcyclohexanecarboximidamide **5b** gave 2-cyclohexylbenzimidazole **6** (R = cyclohexyl) (95%), colourless needles (from MeCN), mp 258–260 °C (lit.,[37] 239–243 °C) (Found: C, 77.7; H, 7.9; N, 14.1. Calc. for $C_{13}H_{16}N_2$: C, 78.0; H, 8.05; N, 14.0%); ν_{max}/cm^{-1} 3070, 2930, 2852, 1448, 1422, 1272, 986, 750; $\delta_H(CF_3CO_2D)$ 1.38–2.29 (m, 10H), 3.23–3.32 (m, 1H), 7.61 (dd, *J* 3.42 and 2.93, 2H), 7.71 (dd, *J* 3.42 and 2.93, 1H); *m/z* 200 ($M^{\bullet+}$).

(b) N^2-Phenylpropionimidamide **5c** gave 2-ethylbenzimidazole **6** (R = Et) (72%), buff plates (from MeCN), mp 173–174.5 °C (lit.,[38,39] 168 °C; 175 °C) (Found: C, 74.2; H, 7.1; N, 19.1. Calc. for $C_9H_{10}N_2$: C, 73.9; H, 6.9; N, 19.2%); ν_{max}/cm^{-1} 2976, 2906, 2834, 1410, 1380, 1324, 1272, 1218, 1032; $\delta_H(CDCl_3$–$[^2H_6]DMSO)$ 1.38 (t, *J* 7.81, 3H), 2.91 (q, *J* 7.81, 2H), 7.12 (dd, *J* 5.86 and 3.42, 2H), 7.81 (dd, *J* 5.86 and 3.42, 2H); *m/z* 146 ($M^{\bullet+}$).

(c) N^2-Phenyl-2,3-dihydro-2-ethylbenzo[*b*]furan-2-carboximidamide **5d** gave 2-(2,3-*dihydro*-2-*ethylbenzo*[b]*furan-2-yl*)-*benzimidazole* **6** (R = 2,3-dihydro-2-ethylbenzo[*b*]furan-2-yl) (67%), needles (from light petroleum, bp 60–80 °C), mp 135 °C (Found: C, 77.5; H, 5.8; N, 10.4. $C_{17}H_{16}N_2O$ requires C, 77.3; H, 6.1; N, 10.6%); ν_{max}/cm^{-1} 2971, 2937, 1598, 1482, 1455, 1422; $\delta_H(CDCl_3)$ 0.97 (t, 3H), 2.30 (m, 2H), 3.50 (d, *J* 16, 1H), 3.87 (d, *J* 16, 1H), 6.8–7.8 (m, 8H), 9.75 (s, 1H); *m/z* 264 ($M^{\bullet+}$).

(d) (N^2-Cyclohexyl)phenylacetimidamide **5e** gave N-*acetyl*-N-*benzyl*-N′-*cyclohexylurea* **11e** (17%), colourless plates (from MeCN), mp 107–109 °C (Found: C, 70.3; H, 8.3; N, 10.2. $C_{16}H_{22}N_2O_2$ requires C, 70.0; H, 8.1; N, 10.2%); ν_{max}/cm^{-1} 3264, 3032, 2934, 2854, 1688, 1508, 1442, 1386, 1342, 1302, 1186; $\delta_H(CDCl_3)$ 1.26–1.99 (m, 10H), 2.19 (s, 3H), 3.76 (m, 1H), 5.03 (s, 2H), 7.17–7.36 (m, 5H), 9.31 (br s, 1H); *m/z* 274 ($M^{\bullet+}$, 5%), 149 (100%) and *N*-benzyl-*N′*-cyclohexylurea **12e** (77%), colourless square plates (from MeCN), mp 150–153.5 °C (lit.,[40] not recorded) (Found: C, 72.5; H, 9.0; N, 12.2. Calc. for $C_{14}H_{20}N_2O$: C, 72.4; H, 8.7; N, 12.1%); ν_{max}/cm^{-1} 3324, 3032, 2928, 2850, 1614, 1444, 1310, 1248, 1066; $\delta_H(CDCl_3)$ 1.01–1.95 (m, 10H), 3.47–3.56 (m, 1H), 4.37 (s, 2H), 7.24–7.37 (m, 5H) (no NH); *m/z* 232 ($M^{\bullet+}$).

(e) N^2-Benzylcyclohexanecarboximidamide **5f** gave *N*-acetyl-*N*-benzyl-*N′*-cyclohexylurea **11e** (27%) and *N*-benzyl-*N′*-cyclohexylurea **12e** (56%), both identical with authentic samples (see above).

(f) N^2-Cyclohexylcyclohexanecarboximidamide **5g** gave *N*-acetyl-*N*,*N′*-dicyclohexylurea **11g** (21%), colourless glassy crystals (from MeCN), mp 125.5–126 °C (lit.,[41,42] 123–126 °C; 125 °C) (Found: C, 67.3; H, 9.7; N, 10.55. Calc. for $C_{15}H_{26}N_2O_2$: C, 67.6; H, 9.8; N, 10.5%); ν_{max}/cm^{-1} 3278, 2938, 2856, 1706, 1636, 1540, 1382, 1336, 1250, 1236; $\delta_H(CDCl_3)$ 1.13–2.04 (m, 20H), 2.20 (s, 3H), 3.64–3.74 (m, 1H), 3.79–3.91 (m, 1H), 7.36 (br s, 1H); *m/z* 266 ($M^{\bullet+}$) together with *N*-cyclohexylacetamide (32%), colourless crystals (from MeCN), mp 104–105 °C (lit.,[43] 107–108 °C) (Found: C, 68.0; H, 10.4; N, 9.8. Calc. for $C_8H_{15}NO$: C, 68.0; H, 10.7; N, 9.9%); ν_{max}/cm^{-1} 3292, 2936, 2854, 1638, 1550, 1442, 1372, 1312, 1114; $\delta_H(CDCl_3)$ 1.03–1.93 (m, 10H), 1.95 (s, 3H), 3.71–3.82 (m, 1H), 5.37 (br s, 1H); *m/z* 141 ($M^{\bullet+}$) and *N*,*N′*-dicyclohexylurea **12g** (28%), colourless needles (from EtOH), mp 231–233 °C (lit.,[44] 232–233 °C) (Found: C, 69.3; H, 10.7; N, 12.5. Calc. for $C_{13}H_{24}N_2O$: C, 69.6; H, 10.8; N, 12.5%); ν_{max}/cm^{-1} 3328, 2930, 2852, 1624, 1568, 1310, 1242, 1086; $\delta_H(CDCl_3$–$[^2H_6]DMSO)$ 1.02–1.92 (m, 20H), 3.49–3.53 (m, 2H), 4.83 (br d, 2H); *m/z* 224 ($M^{\bullet+}$).

(g) N^2-(4-Methylbenzyl)phenylacetimidamide **5h** gave N-*benzyl*-N′-(4-*methylbenzyl*)*urea* **12h** (73%), fine colourless needles (from MeCN), mp 168.5–170 °C (Found: C, 75.3; H, 7.1; N, 11.0. $C_{16}H_{18}N_2O$ requires C, 75.6; H, 7.1; N, 11.0%); ν_{max}/cm^{-1} 3330, 3026, 2920, 2880, 1616, 1562, 1238; $\delta_H(CDCl_3)$ 2.31 (s, 3H), 4.29 (s, 2H), 4.33 (s, 2H), 7.09 (d, *J* 8.42, 2H), 7.15 (d, *J* 8.42, 2H), 7.24–7.33 (m, 5H) (no NH); *m/z* 254 ($M^{\bullet+}$).

(h) N^2-Phenylbenzimidamide **5i** gave N^1-(*N*-phenylcarbamoyl)-N^2-phenylbenzimidamide **13i** (99%), colourless needles (from MeCN), mp 175.5–177.5 °C (lit.,[45] 169–170 °C) (Found: C, 76.3; H, 5.5; N, 13.4. Calc. for $C_{20}H_{17}N_3O$: C, 76.2; H, 5.4; N, 13.3%); ν_{max}/cm^{-1} 3216, 3108, 1678, 1634, 1590, 1546, 1484, 1444, 1290, 1260; $\delta_H(CDCl_3)$ 6.73–7.52 (m, 15 H), 7.99 (br s, 1H), 12.11 (br s, 1H); *m/z* (no $M^{\bullet+}$), 222 (M − 93), 196 (base peak, parent amidine) and acetanilide (80%), colourless needles (from MeCN), mp 112–114.5 °C (lit.,[46] 115 °C) (Found: C, 70.8; H, 6.4; N, 10.6. Calc. for C_8H_9NO: C, 71.1; H, 6.7; N, 10.4%); ν_{max}/cm^{-1} 3298, 3196, 3138, 3060, 1658, 1596, 1546, 1486, 1434, 1366, 1320, 1260; $\delta_H(CDCl_3)$ 2.17 (s, 3H), 7.06–7.13 (m, 1H), 7.26–7.34 (m, 2H), 7.49–7.52 (m, 2H), 8.37 (br s, 1H); *m/z* 135 ($M^{\bullet+}$).

(i) N^2-Phenylfuran-2-carboximidamide **5j** gave N^1-(*N*-phenylcarbamoyl)-N^2-phenylfuran-2-carboximidamide **13j** (99%), colourless needles (from MeCN), mp 168–169 °C, identical with an authentic sample (see below).

(j) N^2-(4-Nitrophenyl)benzimidamide **5k** gave N-*acetyl*-N-(4-*nitrophenyl*)-N′-*phenylurea* **11o** (17%), colourless plates (from MeCN), mp 165.5–167 °C (Found: C, 60.0; H, 4.1; N, 14.0. $C_{15}H_{13}N_3O_4$ requires C, 60.2; H, 4.4; N, 14.0%); $\delta_H(CDCl_3$–$[^2H_6]DMSO)$ 2.04 (s, 3H), 7.29–7.55 (m, 5H), 7.73 (d, *J* 9.16, 2H), 8.20 (d, *J* 9.16, 2H), 11.96 (br s, 1H); *m/z* 299 ($M^{\bullet+}$) together with 4-nitroacetanilide (17%), colourless crystals (from MeCN), mp 213–215 °C (lit.,[47] 214–215 °C) (Found: C, 53.1; H, 4.4; N, 15.5. Calc. for $C_8H_8N_2O_3$: C, 53.3; H, 4.5; N, 15.55%); ν_{max}/cm^{-1} 3344, 3100, 1676, 1596, 1544, 1494, 1330, 1302, 1254, 1110; $\delta_H(CDCl_3$–$[^2H_6]DMSO)$ 2.17 (s, 3H), 7.84 (d, *J* 9.28, 2H), 8.14 (d, *J* 9.28, 2H), 10.27 (br s, 1H); *m/z* 180 ($M^{\bullet+}$) and N^1-(*N*-phenylcarbamoyl)-N^2-(4-nitrophenyl)benzimidamide **14k** (56%), pale yellow needles (from MeCN), mp 177–180 °C, identical with an authentic sample (see below).

(k) N^2-Phenyl-4-methoxybenzimidamide **5l** gave N^1-(N-*phenylcarbamoyl*)-N^2-*phenyl*-4-*methoxybenzimidamide* **13l** (90%), colourless needles (from MeCN), mp 174–175.5 °C (Found: C, 73.1; H, 5.6; N, 12.4. $C_{21}H_{19}N_3O_2$ requires C, 73.0; H, 5.5; N, 12.2%); ν_{max}/cm^{-1} 3436, 3220, 2964, 1694, 1600, 1564, 1496, 1448, 1310, 1270, 1248, 1180; δ_H($CDCl_3$) 3.77 (s, 3H), 6.73–6.79 (m, 3H), 6.82 (d, *J* 9.28, 2H), 6.93–7.37 (m, 7H), 7.40 (d, *J* 9.28, 2H), 7.45–7.51 (m, 1H), 8.60 (br s, 1H), 12.10 (br s, 1H); *m/z* 253 (M − 92, PhNH) and *N*-(4-methoxyphenyl)-acetamide (85%), colourless needles (from MeCN), mp 128–129.5 °C (lit.,[48] 130–132 °C) (Found: C, 65.8; H, 6.5; N, 8.3. Calc. for $C_9H_{11}NO_2$: C, 65.4; H, 6.7; N, 8.5%); ν_{max}/cm^{-1} 3250, 3128, 3072, 2962, 2836, 1652, 1608, 1512, 1246, 1030; δ_H($CDCl_3$) 2.13 (s, 3H), 3.77 (s, 3H), 6.84 (d, *J* 9.27, 2H), 7.39 (d, *J* 9.27, 2H); *m/z* 165 ($M^{\bullet+}$).

(l) N^2-Cyclohexylbenzimidamide **5m** gave N^1-(N-*cyclohexylcarbamoyl*)-N^2-*cyclohexylbenzimidamide* **13m** (96%), colourless plates (from MeCN), mp 137–140 °C (Found: C, 73.1; H, 9.1; N, 12.65. $C_{20}H_{29}N_3O$ requires C, 73.4; H, 8.9; N, 12.8%); ν_{max}/cm^{-1} 3210, 3112, 2930, 2852, 1674, 1642, 1548, 1490, 1446, 1276, 1244, 1074; δ_H($CDCl_3$) 1.11–1.97 (m, 20H), 3.22 (m, 1H), 3.64 (m, 1H), 5.49 (br s, 1H), 7.41 (m, 5H), 10.69 (br s, 1H); *m/z* (no $M^{\bullet+}$), 229 (M − NHC_6H_{11}) and acetanilide (99%).

(ii) At 80 °C. Using a procedure identical to that described above, except that the reaction flask was maintained at 80 °C using a regulated bath throughout the addition, N^2-phenylbenzimidamide **5i** gave *N*-acetyl-*N*,*N*′-diphenylurea **11i** (75%), colourless glassy plates (from MeCN), mp 105–105.5 °C (lit.,[41,49] 102–104 °C, 106 °C) (Found: C, 70.9; H, 5.3; N, 11.1. Calc. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.0%); ν_{max}/cm^{-1} 3184, 3062, 1718, 1662, 1588, 1530, 1488, 1440, 1368, 1266, 1224, 1166; δ_H($CDCl_3$) 1.98 (s, 3H), 7.04–7.11 (m, 1H), 7.26–7.32 (m, 4H), 7.44–7.57 (m, 5H), 11.47 (br s, 1H); *m/z* 254 ($M^{\bullet+}$) and 2-phenylbenzimidazole **6** (R = Ph) (9%), mp 288–291 °C (lit.,[50] 289–291 °C) (Found: C, 80.5; H, 5.0; N, 14.6. Calc. for $C_{13}H_{10}N_2$: C, 80.4; H, 5.2; N, 14.4%); ν_{max}/cm^{-1} 3432, 3048, 1586, 1532, 1474, 1458, 1440, 1406, 1312, 1274; δ_H($CDCl_3$–[$^2H_6$]DMSO) 7.24–7.29 (m, 2H), 7.43–7.81 (m, 5H), 8.12–8.15 (m, 2H), 10.93 (br s, 1H); *m/z* 194 ($M^{\bullet+}$).

In a similar manner the following transformations were achieved.

(a) N^2-Phenylfuran-2-carboximidamide **5j** gave N-*acetyl*-N-(2-*furyl*)-N′-*phenylurea* **11j** (67%), colourless crystals (from MeCN), mp 107–109 °C (Found: C, 64.2; H, 4.8; N, 11.7. $C_{13}H_{12}N_2O_3$ requires C, 63.9; H, 4.95; N, 11.5%); ν_{max}/cm^{-1} 3206, 3134, 1718, 1596, 1544, 1498, 1444, 1424, 1370, 1270, 1216, 1178; δ_H(60 MHz, $CDCl_3$) 1.99 (s, 3H), 6.2–6.5 (m, 2H), 6.9–7.6 (m, 6H), 10.6 (br s, 1H); *m/z* 244 ($M^{\bullet+}$).

(b) (N^2-Cyclohexyl)phenylacetimidamide **5e** gave *N*-benzyl-*N*′-cyclohexylurea **12e** (83%), identical with an authentic sample (see above).

(c) N^2-Cyclohexylcyclohexanecarboximidamide **5g** gave *N*,*N*′-dicyclohexylurea **12g** (68%), identical with an authentic sample (see above).

(iii) At 50 °C. Using a procedure analogous to that described above N^2-phenylbenzimidamide **5i** gave *N*-acetyl-*N*,*N*′-diphenylurea **11i** (65%) and 2-phenylbenzimidazole **6** (R = Ph) (16%); both products were identical to authentic samples.

(iv) At 25 °C. Using a procedure analogous to that described above but using CH_2Cl_2 as solvent N^2-phenylbenzimidamide **5i** gave *N*,*N*-diphenylcarbodiimide **9i** (30%), colourless crystals, mp 163–166 °C (trimer) (lit.,[51] 168–170 °C) (Found: C, 80.6; H, 5.1; N, 14.4. Calc. for $C_{13}H_{10}N_2$: C, 80.4; H, 5.2; N, 14.4%); ν_{max}(thin film)/cm^{-1} 3060, 2138, 1656, 1588, 1484, 1306, 1206; δ_H($CDCl_3$) 7.08–7.16 (m, 3H), 7.22–7.29 (m, 2H); *m/z* 194 ($M^{\bullet+}$ monomer), *N*,*N*′-diphenylurea **12i** (26%), colourless crystals (from EtOH), mp 242–243 °C (lit.,[52,53] 242–244 °C; 235 °C), identical with an authentic sample, and N^2-phenylbenzamidin-N^2-ium acetate (39%), colourless crystals (from EtOH), mp 100–104 °C, identical with an authentic sample (see below).

Reaction of amidines with bis(trifluoroacetoxy)iodobenzene (BFIB)

***N*-2-Phenylbenzimidamide 5i.** Using a procedure identical to that described for reaction with DAIB, compound **5i** was treated with BFIB in toluene at 110 °C. Upon standing at room temperature, a solid separated from the reaction mixture and was identified as 2-phenylbenzimidazol-1-ium trifluoroacetate (28%), a buff powder, mp 195–199.5 °C; ν_{max}/cm^{-1} 3072, 2942, 2624 (br), 1656, 1428, 1394, 1206, 1180, 1122; δ_H([$^2H_6$]DMSO) 7.51 (dd, *J* 5.86 and 6.35, 2H), 7.69–7.72 (m, 3H), 7.84 (dd, *J* 5.86 and 6.34, 2H), 8.25–8.29 (m, 2H), 12.47 (br s, 2H); δ_F([$^2H_6$]DMSO) −75.82 (s); *m/z* 194/195 (benzimidazole $M^{\bullet+}$, M + 1), 97 ($COCF_3$). This material (0.15 g, 0.5 mmol) was shaken with 30% aqueous sodium hydroxide (10 cm^3), extracted with chloroform and dried ($NaSO_4$). Evaporation gave a solid that was washed with diethyl ether, air-dried and identified as 2-phenylbenzimidazole **6** (R = Ph) (0.08 g) (80%), identical with an authentic sample. Chromatotron chromatography of the mother liquor gave *N*-phenyltrifluoroacetamide (28%), mp 77–83 °C, colourless crystals (from CH_2Cl_2); ν_{max}/cm^{-1} 3322, 1700, 1600, 1546, 1448, 1286, 1242, 1250; *m/z* 189 ($M^{\bullet+}$) and N^2-phenylbenzamidin-N^2-ium trifluoroacetate (33%), colourless needles (from CH_2Cl_2), mp 120–127 °C, identical with an authentic sample.

When the reaction was repeated at 80 °C the following products were isolated in a similar manner and shown to be identical to authentic samples: 2-phenylbenzimidazol-3-ium trifluoroacetate (22%), *N*,*N*′-diphenylurea **12i** (17%) and N^2-phenylbenzamidin-N^2-ium trifluoroacetate (53%).

In a similar manner N^2-cyclohexylcyclohexanecarboximidamide **5g** at 110, 80 and 25 °C gave only N^2-cyclohexylcyclohexanecarboxamidin-N^2-ium trifluoroacetate (59, 68 and 65% yield respectively), colourless crystals, mp 203–205.5 °C, identical with an authentic sample (see below).

Reaction of amidines with lead tetraacetate (LTA)

***N*^{2}-Phenylbenzimidamide 5i.** The reaction procedure was identical to that described using DAIB at 110 °C. The mother liquor was filtered through Celite to remove insoluble lead salts before evaporation. Purification by chromatography gave 2-phenylbenzimidazole **6** (R = Ph) (86%), identical to an authentic sample. The same product **6** (R = Ph) (70%) was obtained when the reaction was carried out at 80 °C.

In a similar manner N^2-phenylfuran-2-carboximidamide **5j** at 110 °C gave 2-(2-furyl)benzimidazole **6** (R = 2-furyl) (65%), buff powder (from MeCN), mp 234–236 °C (lit.,[54] 287 °C†); ν_{max}/cm^{-1} 3436, 3058, 2664, 1628, 1522, 1442, 1412, 1364, 1276, 1232, 1012; δ_H($CDCl_3$–[$^2H_6$]DMSO) 6.57–6.58 (m, 1H), 7.20–7.28 (m, 5H), 7.55–7.56 (m, 1H), 11.37 (br s, 1H); *m/z* 184 ($M^{\bullet+}$, base).

Thermolysis of *N*-acetyl-*N*-(2-furyl)-*N*′-phenylurea 11j

A mixture of compound **11j** (0.224 g, 1 mmol) and freshly distilled aniline (0.093 g, 1 mmol) in toluene (10 cm^3) was stirred in an oil bath at 110 °C and maintained under reflux (20 min). The mixture was allowed to cool to room temperature and the solid that separated was collected, recrystallised from ethanol and identified as *N*,*N*′-diphenylurea (0.20 g, 94%). The yellow filtrate was evaporated to give a solid which was recrystallised from acetonitrile and identified as N-(2-*furyl*)*acetamide* **15** (0.11 g, 88%), buff needles, mp 111–113 °C (Found: C, 57.9; H, 5.3; N, 11.0. $C_6H_7NO_2$ requires C, 57.6; H, 5.6; N, 11.2%); ν_{max}/cm^{-1} 3200, 3042, 2836, 1656, 1610, 1566, 1366, 1280, 1232, 1216, 1148, 1068; δ_H($CDCl_3$) 2.16 (s, 3H), 6.30 (d, *J* 0.9, 1H), 6.34–6.35 (m, 1H), 7.02–7.03 (m, 1H); *m/z* 125 ($M^{\bullet+}$).

† The difference between the experimental and literature values is presumed to result from polymorphism in the compound.

Preparation of N^1-(*N*-phenylcarbamoyl)-N^2-phenylfuran-2-carboximidamide 13j

A solution of phenyl isocyanate (0.11 cm^3, 1 mmol) in dry chloroform (5 cm^3) was added to N^2-phenylfuran-2-carboximidamide **5j** (0.186 g, 1 mmol) in chloroform (8 cm^3). The solvent was partially evaporated giving a solid that was collected, recrystallised from acetonitrile and identified as *compound* **13j** (0.302 g, 99%), colourless needles, mp 167–169 °C (Found: C, 71.0; H, 4.8; N, 13.95. $C_{18}H_{15}N_3O_2$ requires C, 70.8; H, 4.95; N, 13.8%); ν_{max}/cm^{-1} 3274, 3126, 3024, 1690, 1630, 1592, 1550, 1484, 1444, 1286, 1272; $\delta_H(CDCl_3)$ 5.73 (s, 1H), 6.28 (s, 1H), 6.91–7.57 (m, 11H), 7.87 (br s, 1H), 11.71 (br s, 1H); *m/z* 305 ($M^{\bullet+}$).

Preparation of N^1-(*N*-phenylcarbamoyl)-N^2-(4-nitrophenyl)-benzimidamide 14k

A solution of phenyl isocyanate (0.087 g, 0.7 mmol) in acetonitrile (30 cm^3) was stirred with N^2-(4-nitrophenyl)-benzimidamide **5k** (0.176 g, 0.7 mmol) at room temperature for 5 min. The solid precipitate that formed was recrystallised from acetonitrile and identified as *compound* **14k** (0.2 g, 79%), colourless needles, mp 176–178 °C (Found: C, 66.75; H, 4.4; N, 15.7. $C_{20}H_{16}N_4O_3$ requires C, 66.7; H, 4.5; N, 15.55%); ν_{max}/cm^{-1} 3214, 3096, 1684, 1628, 1582, 1496, 1334, 1264, 1104; $\delta_H([^2H_6]DMSO)$ 6.93–7.69 (m, 10H), 8.08 (d, *J* 8.79, 2H) and 8.26 (d, *J* 8.79, 2H), 9.65 (s, 1H), 10.22 (s, 1H); *m/z* 360 ($M^{\bullet+}$).

Preparation of amidine salts

(N^2-Phenyl)phenylacetamidin-N^2-ium toluene-*p*-sulfonate. To a stirred solution of (N^2-phenyl)phenylacetimidamide **5a** (1.05 g, 5 mmol) in acetonitrile (30 cm^3) at room temperature was added a solution of toluene-*p*-sulfonic acid monohydrate (0.95 g, 5 mmol) in acetonitrile (15 cm^3). Diethyl ether (30 cm^3) was added and the solution refrigerated (24 h). The solid precipitate was recrystallised from acetonitrile and identified as (N²-*phenyl*)*phenylacetamidin*-N²-*ium toluene*-p-*sulfonate* (1.1 g, 58%), colourless needles, mp 136–137.5 °C (Found: C, 66.1; H, 5.6; N, 7.3. $C_{21}H_{22}N_2SO_3$ requires C, 65.95; H, 5.8; N, 7.3%); ν_{max}/cm^{-1} 3141, 3062, 2961, 2906, 1679, 1633, 1593, 1493, 1452, 1178, 1119, 1030, 1007; $\delta_H(CDCl_3$–$[^2H_6]DMSO)$ 2.33 (s, 6H), 3.81 (s, 2H), 4.09 (s, 2H), 6.93–7.73 (m, 10ArH + 1NH), 9.14 (br s, 1H), 9.65 (br s, 1H), 9.91 (br s, 1H), 11.57 (br s, 1H), 11.67 (br s, 1H).

N^2-Phenylbenzamidin-N^2-ium acetate. N^2-Phenylbenzimidamide **5i** (0.1 g, 5 mmol) was dissolved in glacial acetic acid. After refrigeration for several days the solid that had formed was recrystallised from ethanol and identified as N^2-phenylbenzamidin-N^2-ium acetate (0.12 g, 99%), mp 100–104 °C; ν_{max}/cm^{-1} 2848 (br), 1656, 1594, 1542, 1480, 1442, 1404, 1262, 1102; $\delta_H(CDCl_3)$ 1.98 (s, 3H), 6.92–7.52 (m, 11H), 7.58 (br s, 2H); *m/z* 196/197 (amidine $M^{\bullet+}$, M + 1), 43 (Ac).

N^2-Cyclohexylcyclohexanecarboxamidin-N^2-ium trifluoroacetate. N^2-Cyclohexylcyclohexanecarboximidamide **5g** (0.8 g, 4 mmol) was dissolved in trifluoroacetic acid. Addition of a small amount of water gave a solid precipitate that was recrystallised from acetonitrile and identified as N²-*cyclohexylcyclohexanecarboxamidin*-N²-*ium trifluoroacetate* (0.8 g, 62%), colourless crystals, mp 204–208 °C (Found: C, 55.8; H, 7.9; N, 8.8. $C_{15}H_{25}N_2O_2F_3$ requires C, 55.9; H, 7.8; N, 8.7%); ν_{max}/cm^{-1} 3096, 2936, 2864, 1666, 1628, 1204, 1178, 1132; $\delta_H([^2H_6]DMSO)$ 1.14–1.80 (m, 20H), 2.30–2.45 (m, 1H), 3.46 (m, 1H), 8.68 (br s, 2H), 8.99 (br s, 1H); $\delta_F(CDCl_3$–$[^2H_6]DMSO)$ −75.31 ppm (s); *m/z* 208/209 (amidine $M^{\bullet+}$, M + 1), 97 ($COCF_3$), 83 (cyclohexyl).

A similar procedure using N^2-phenylbenzimidamide **5i** (0.1 g, 0.5 mmol) gave N^2-phenylbenzamidin-N^2-ium trifluoroacetate (0.12 g, 80%), small colourless needles (from EtOH), mp 126–129 °C; ν_{max}/cm^{-1} 3322, 3056, 1676, 1596, 1488, 1432, 1186, 1136; $\delta_H(CDCl_3$–$[^2H_6]DMSO)$ 6.89–8.00 (m, 10H), 9.52, 11.37 and 13.5 (each br s, 1H); $\delta_F([^2H_6]DMSO)$ −75.82 ppm (s); *m/z* 196 (amidine $M^{\bullet+}$), 97 ($COCF_3$).

Preparation of N^1,N^2-diphenyl[phenyl(phenylimino)methylamino]formamidin-N^2-ium toluene-*p*-sulfonate 3. A solution of diphenylcarbodiimide[55] (1.95 g, 10 mmol) in ethanol (5 cm^3) was stirred and heated under reflux and a solution of N^2-phenylbenzamidine **5i** (1.96 g, 10 mmol) in ethanol (20 cm^3) was added dropwise. After addition was complete (30 min), reflux was maintained (60 min) and toluene-*p*-sulfonic acid monohydrate (1.9 g, 10 mmol) in ethanol (10 cm^3) was added dropwise. Evaporation gave a clear orange oil that was dissolved in diethyl ether (10 cm^3) and the solution was refrigerated overnight. The crystalline product was collected, recrystallised from ethanol and identified as N¹,N²-*diphenyl*[*phenyl*(*phenylimino*)-*methylamino*]*formamidin*-N²-*ium toluene*-p-*sulfonate* **3** (2.3 g, 41%), buff crystals, mp 197–200 °C (Found: C, 70.2; H, 5.3; N, 9.95. $C_{33}H_{30}N_4O_3S$ requires C, 70.4; H, 5.4; N, 10.0%); ν_{max}/cm^{-1} 3459, 3212, 3026, 2967, 1570, 1484, 1444, 1350, 1210, 1120; $\delta_H(CDCl_3)$ 2.27 (s, 3H), 6.78 (d, 2H), 6.94–7.76 (m, 20H), 7.84 (d, 2H), 9.82 (s, 1H), 10.29 (s, 2H); *m/z* 390 (amidine $M^{\bullet+}$).

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