New Synthetic Route to *N,N'*-Diaminohydantoins from Hydrazido Pyridinium Salts

Claudie Florac, Philippe Le Grel, Michèle Baudy-Floc'h and Albert Robert*
Groupe de Recherches de Chimie Structurale, Unité de Recherches associée au C.N.R.S., U.R.A. DO704, Université de Rennes, Campus de Beaulieu, F-35042 Rennes Cédex, France

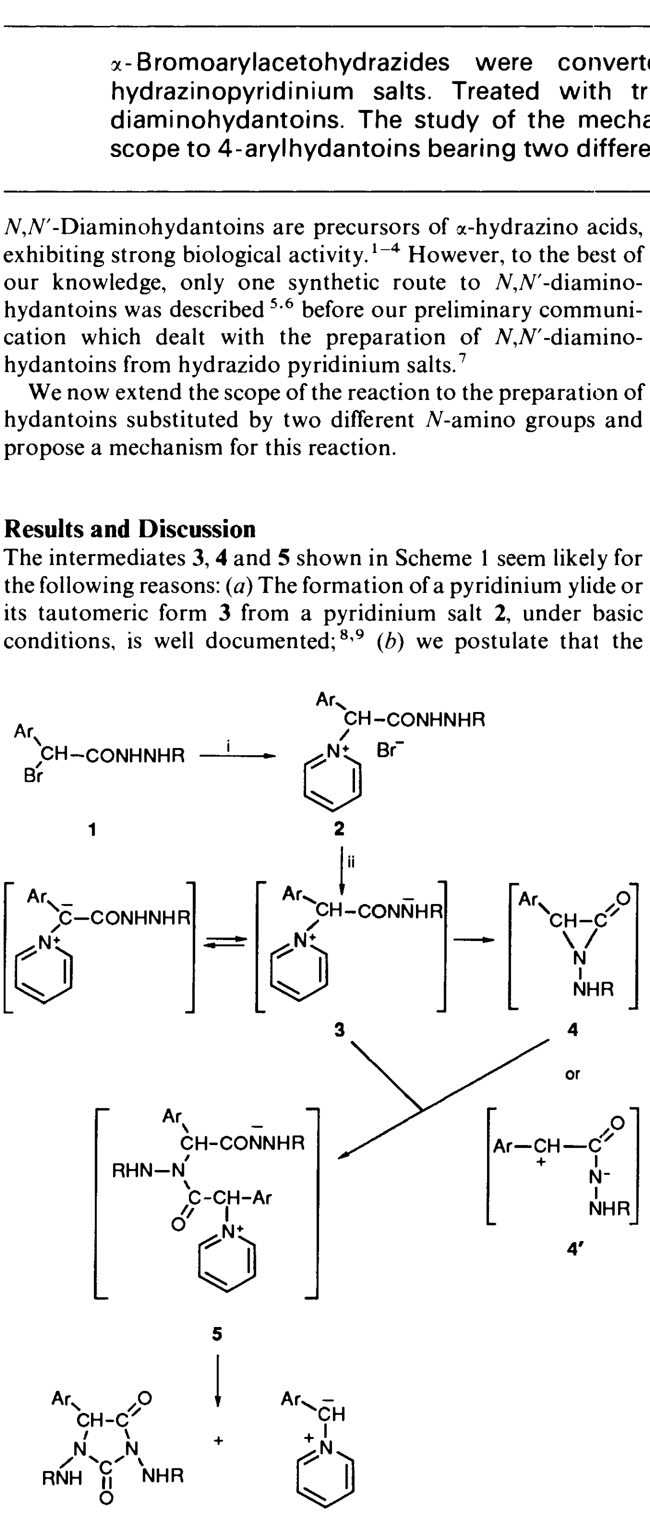
α-Bromoarylacetohydrazides were converted by pyridine into the corresponding arylacetylhydrazinopyridinium salts. Treated with triethylamine, these pyridinium salts afford 4-aryl-1,3-diaminohydantoins. The study of the mechanism of this unexpected reaction lead us to extend its scope to 4-arylhydantoins bearing two different substituted amino groups on nitrogens 1 and 3.

N,N'-Diaminohydantoins are precursors of α-hydrazino acids, exhibiting strong biological activity.[1–4] However, to the best of our knowledge, only one synthetic route to *N,N'*-diaminohydantoins was described[5,6] before our preliminary communication which dealt with the preparation of *N,N'*-diaminohydantoins from hydrazido pyridinium salts.[7]

We now extend the scope of the reaction to the preparation of hydantoins substituted by two different *N*-amino groups and propose a mechanism for this reaction.

Results and Discussion

The intermediates **3**, **4** and **5** shown in Scheme 1 seem likely for the following reasons: (*a*) The formation of a pyridinium ylide or its tautomeric form **3** from a pyridinium salt **2**, under basic conditions, is well documented;[8,9] (*b*) we postulate that the pyridinium betaine **3** cyclizes into the *N*-aminoaziridinone **4** or, as suggested by one referee, its opened form **4'**. The elimination of pyridine during the course of this reaction is similar to the elimination of a halide ion in the Favorskii rearrangement where a zwitterionic opened cyclopropanone has been proposed.[10] The elimination of pyridine from **2** is also similar to the elimination of a bromide ion from **1** (Ar = *p*-ClC_6H_4, R = COPh) in basic media. Whilst not isolated, the formation of an *N*-aminoaziridinone intermediate **4** (Ar = *p*-ClC_6H_4, R = COPh) is observed by ^1H NMR as a labile intermediate.[11] The appearance of a signal at δ 5.80 is more attributable to **4** than to the opened form **4'**. Nevertheless **4'** may be the reactive intermediate trapped by nucleophilic reagents. However, we have not been able to trap the dipole **4'** by dipolarophilic reagents. In fact, we observed that like **1**, the hydrazidopyridinium salt **2** (Ar = *p*-MeC_6H_4, R = CO_2Me) reacted with methanol in the presence of triethylamine to give **8** (Ar = *p*-MeC_6H_4, R = CO_2Me) (Scheme 2). (*c*) The reaction between the aziridinone **4** or the dipolar form **4'** and the betaine **3** is the expected nucleophilic addition,[11] leading to the adduct **5**. The formation of such an intermediate **5** was proved for **5** (Ar = *p*-MeC_6H_4, R = COPh) which was stable enough to be isolated as a salt and characterized by ^1H NMR and IR spectra (Experimental section). We further demonstrated that **5** HBr (Ar = *p*-MeC_6H_4, R = COPh) gave the *N*-aminohydantoin **6** (Ar = *p*-MeC_6H_4, R = COPh) when treated with triethylamine in boiling acetonitrile.



Scheme 1 *Reagents and conditons:* i, C_5H_5N (3 equiv.), MeCN, reflux, 4 h; ii, NEt_3 (2 equiv.), MeCN, reflux, 4 h

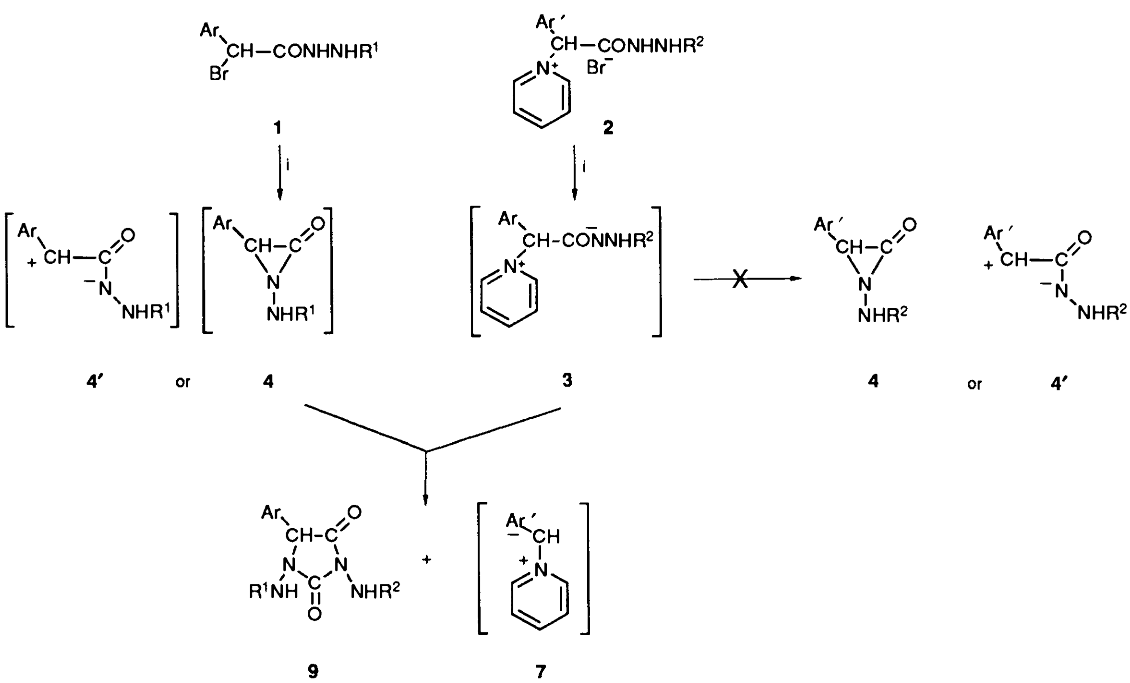
$$\mathbf{2} \xrightarrow{\text{i}} \mathbf{4} \text{ or } \mathbf{4'} \xrightarrow{\text{ii}} \text{ArCH(OMe)CONHNHR}$$

8

(Ar = *p*-MeC_6H_4, R = CO_2Me)

Scheme 2 *Reagents and conditions:* i, NEt_3 (1 equiv.); ii, MeOH, reflux, 1 h

The key step in Scheme 1 is the nucleophilic ring opening of the aziridinone **4** by the betaine **3**. Furthermore, **3** and **4** arise from the same starting pyridinium salt **2**. As aziridinone **4** can also be generated from α-halogenohydrazide **1**,[11] and as bromide is a better leaving group than pyridine, we postulate that by mixing the α-bromohydrazide **1** and the hydrazidopyridinium salt **2** in the presence of triethylamine, the betaine **3** will be formed exclusively from **2** while the aziridinone **4** will arise mostly from the α-bromohydrazide derivative **1** (Scheme 3). To check the validity of this and also to prepare hydantoins substituted by two different amino groups, the reactions described in Scheme 3 were performed, and the results were in perfect agreement with our proposed mechanism. Note that the aryl substituent in the obtained hydantoin **9** comes from the starting α-bromohydrazide **1** while the N–NHR[2] fragment



Scheme 3 *Reagents and conditions:* i, NEt_3 (2 equiv.), MeCN, reflux, 4 h

arises from the pyridinium salt **2**. The pyridinium ylide **7** eliminated in the last step of the reaction is not stable enough to be isolated and characterized.

Conclusions

As our starting materials, the α-halogenohydrazides **1**, are easily prepared from *gem* dicyano epoxides,[12] the described reaction is a convenient route to *N*,*N*′-diaminohydantoins. The analysis of the mechanism of this unexpected reaction leads to hydantoins substituted in a predictable manner, by two different *N*-amino groups.

Experimental

^1H NMR spectra were recorded at 80 MHz on a Bruker WP 80 spectrometer and ^{13}C NMR spectra at 75 MHz on Bruker AM 300 spectrometer with tetramethylsilane as internal reference. Mass spectra were determined with a Varian Mat 311 spectrometer. IR spectra were determined with a Perkin-Elmer 225 or 1420 spectrometer. M.p.s were measured on a Kofler hot-stage apparatus.

Hydrazino Pyridinium Salts **2**.—α-Halogenohydrazide **1** (10 mmol) and pyridine (30 mmol) were allowed to react in boiling MeCN (50 cm^3). After the mixture had been cooled at room temperature, the precipitated salt **2** was recovered and recrystallized from ethanol (R = COPh, COMe) or from methanol (R = CO_2Me).

N-[α-(*Benzoylhydrazinocarbonyl*)*benzyl*]*pyridinium bromide*. **2** (Ar = C_6H_5, R = COPh). Yield 80%; m.p. 235 °C (Found: C, 58.6; H, 4.35; Br, 19.3; N, 9.85. $C_{20}H_{18}BrN_3O_2$ requires C, 58.26; H, 4.37; Br, 19.42; N, 10.19%); ν_{max}(Nujol)/cm^{-1} 3150m (NH), 1712s and 1660s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 7.57 (11 H, m, ArCH),[13] 7.97 (2 H, t, C_5H_5N), 8.47 (1 H, t, C_5H_5N) and 8.97 (2 H, d, C_5H_5N.

N-[α-(*Benzoylhydrazinocarbonyl*)-p-*methylbenzyl*]*pyridinium bromide*. **2** (Ar = *p*-MeC_6H_4, R = COPh). Yield 84%; m.p. >260 °C (Found: C, 59.55; H, 4.7; Br, 18.47; N, 9.9. $C_{21}H_{20}BrN_3O_2$ requires C, 59.15; H, 4.69; Br, 18.78; N, 9.86%); ν_{max}(Nujol)/cm^{-1} 3160br (NH), 1715s and 1678s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 2.37 (3 H, s, Me), 7.57 (10 H, m, ArCH), 7.98 (2 H, t, C_5H_5N), 8.49 (1 H, t, C_5H_5N) and 8.97 (2 H, d, C_5H_5N).

N-[α-(*Benzoylhydrazinocarbonyl*)-p-*chlorobenzyl*]*pyridinium bromide*. **2** (Ar = *p*-ClC_6H_4, R = COPh). Yield 70%, m.p. >260 °C (Found: C, 54.05; H, 3.8; Br, 17.51; Cl, 8.11; N, 9.4; M^+, 365.976. $C_{20}H_{17}BrClN_3O_2$ requires C, 53.75; H, 3.80; Br 17.91; Cl, 7.95; N, 9.40%; *M*, 365.9770); ν_{max}(Nujol)/cm^{-1} 3160br (NH), 1715s and 1671s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 7.59 (10 H, m, ArCH), 8.06 (2 H, t, C_5H_5N), 8.55 (1 H, t, C_5H_5N) and 8.97 (2 H, d, C_5H_5N).

N-[α-(*Benzoylhydrazinocarbonyl*)-o-*chlorobenzyl*]*pyridinium bromide*. **2** (Ar = *o*-ClC_6H_4, R = COPh). Yield 90%, m.p. >260 °C (Found: C, 53.9; H, 3.75; Br, 17.61; Cl, 8.03; N, 9.35; M^+, 365.976). $C_{20}H_{17}N_3O_2BrCl$ requires C, 53.75; H, 3.80; Br, 17.91; Cl, 7.95; N, 9.40%; *M*, 365.9770); ν_{max}(Nujol)/cm^{-1} 3120br (NH), 1717s and 1665s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 7.65 (10 H, m, ArCH), 8.02 (2 H, t, C_5H_5N), 8.55 (1 H, t, C_5H_5N) and 8.95 (2 H, d, C_5H_5N).

N-[α-(*Benzoylhydrazinocarbonyl*)-p-*nitrobenzyl*]*pyridinium bromide*. **2** (Ar = *p*-$NO_2C_6H_4$, R = COPh). Yield 71%, m.p. >260 °C (Found: C, 52.45; H, 3.85; Br, 17.5; N, 11.9. $C_{20}H_{17}BrN_4O_4$ requires C, 52.63; H, 3.73; Br, 17.32; N, 12.29%); ν_{max}(Nujol)/cm^{-1} 3140br (NH), 1713s and 1655s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 7.75 (10 H, m, ArCH), 8.27 (2 H, t, C_5H_5N), 8.67 (1 H, t, C_5H_5N) and 9.15 (2 H, d, C_5H_5N).

N-[α-(*Benzoylhydrazinocarbonyl*)-2,4-*dichlorobenzyl*]*pyridium bromide*. **2** (Ar = 2,4-$Cl_2C_6H_3$, R = COPh). Yield 85%, m.p. 224 °C (Found: C, 49.85; H, 3.4; Br, 16.5; Cl, 14.35; N, 8.7. $C_{20}H_{16}BrCl_2N_3O_2$ requires C, 49.90; H, 3.33; Br 16.63; Cl, 14.76; N, 8.73%); ν_{max}(Nujol)/cm^{-1} 3160br (NH), 1710s and 1655s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 7.50 (9 H, m, ArCH), 7.95 (2 H, t, C_5H_5N), 8.61 (1 H, t, C_5H_5N) and 8.87 (2 H, d, C_5H_5N).

N-[α-(*Benzoylhydrazinocarbonyl*)-2,3-*dichlorobenzyl*]*pyridinium bromide*. **2** (Ar = 2,3-$Cl_2C_6H_3$, R = COPh). Yield 90%, m.p. >260 °C (Found: C, 49.55; H, 3.3; Br, 16.35; Cl, 14.8; N, 8.4. $C_{20}H_{16}BrCl_2N_3O_2$ requires C, 49.90; H, 3.33; Br 16.63; Cl, 14.76; N, 8.73%); ν_{max}(Nujol)/cm^{-1} 3140br (NH), 1718s and 1668s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 7.78 (9 H, m, ArCH), 8.05 (2 H, t, C_5H_5N), 8.55 (1 H, t, C_5H_5N) and 8.97 (2 H, d, C_5H_5N).

N-[α-(*Benzoylhydrazinocarbonyl*)-3,4-*dichlorobenzyl*]*pyridinium bromide*. **2** (Ar = 3,4-$Cl_2C_6H_3$, R = COPh). Yield 85%, m.p. 260 °C (Found: C, 49.85; H, 3.3; Br, 16.45; Cl, 14.65; N, 8.6. $C_{20}H_{16}BrCl_2N_3O_2$ requires C, 49.90; H, 3.33; Br 16.63; Cl, 14.76; N, 8.73%); ν_{max}(Nujol)/cm^{-1} 3130br (NH), 1715s and 1678s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 7.52 (9 H, m, ArCH), 8.01 (2 H, t, C_5H_5N), 8.50 (1 H, t, C_5H_5N) and 9.07 (2 H, d, C_5H_5N).

N-[α-(*Acetylhydrazinocarbonyl*)-o-*chlorobenzyl*]*pyridinium bromide*. **2** (Ar = *o*-ClC_6H_4, R = COMe). Yield 80%, m.p. 244 °C (Found: C, 46.6; H, 3.85; Br, 20.41; Cl, 9.25; N, 10.9. $C_{15}H_{15}BrClN_3O_2$ requires C, 46.81; H, 3.90; Br 20.81; Cl, 9.23; N, 10.92%); ν_{max}(Nujol)/cm^{-1} 3160br (NH), 1718s and 1682s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 2.20 (3 H, s, Me), 7.50 (5 H, m, ArCH), 8.20 (2 H, t, C_5H_5N), 8.60 (1 H, t, C_5H_5N) and 8.95 (2 H, d, C_5H_5N).

N-[α-(*Acetylhydrazinocarbonyl*)-2,3-*dichlorobenzyl*]*pyridinium bromide*. **2** (Ar = 2,3-$Cl_2C_6H_3$, R = COMe). Yield 90%, m.p. >260 °C (Found: C, 42.55; H, 3.3; Br, 18.8; Cl, 16.95; N, 6.55. $C_{15}H_{14}BrCl_2N_3O_2$ requires C, 42.96; H, 3.34; Br 19.09; Cl, 16.94; N, 6.68%); ν_{max}(Nujol)/cm^{-1} 3120br (NH); 1720s and 1680s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 2.30 (3 H, s, Me), 7.72 (4 H, m, ArCH), 8.20 (2 H, t, C_5H_5N), 8.66 (1 H, t, C_5H_5N) and 8.95 (2 H, d, C_5H_5N).

N-[α-(*Methoxycarbonylhydrazinocarbonyl*)*benzyl*]*pyridinium bromide*. **2** (Ar = C_6H_5, R = CO_2Me). Yield 65%, m.p. 152 °C (Found: C, 49.0; H, 4.35; Br, 21.45; N, 11.65. $C_{15}H_{16}BrN_3O_3$ requires C, 49.18; H, 4.37; Br 21.86; N, 11.47%); ν_{max}(Nujol)/cm^{-1} 3130br (NH), 1735s and 1695s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 3.75 (3 H, s, Me), 7.55 (6 H, m, ArCH), 8.02 (2 H, t, C_5H_5N), 8.55 (1 H, t, C_5H_5N) and 8.97 (2 H, d, C_5H_5N).

N-[α-*Methoxycarbonylhydrazinocarbonyl*)-p-*methylbenzyl*]*pyridinium bromide*. **2** (Ar = *p*-MeC_6H_4, R = CO_2Me). Yield 92%, m.p. 234 °C (Found: C, 50.8; H, 4.7; Br, 21.35; N, 11.45. $C_{16}H_{18}BrN_3O_3$ requires C, 50.53; H, 4.74; Br 21.05; N, 11.05%); ν_{max}(Nujol)/cm^{-1} 3170br (NH), 1741s and 1705s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 2.40 (3 H, s, Me), 3.80 (3 H, s, CO_2Me), 7.40 (5 H, m, ArCH), 8.04 (2 H, t, C_5H_5N), 8.55 (1 H, t, C_5H_5N) and 8.92 (2 H, d, C_5H_5N).

N-[α-(*Methoxycarbonylhydrazinocarbonyl*)-p-*chlorobenzyl*]*pyridinium bromide*. **2** (Ar = *p*-ClC_6H_4, R = CO_2Me). Yield 80%, m.p. 252 °C (Found: C, 44.85; H, 3.65; Br, 19.55; Cl, 8.9; N, 10.4. $C_{15}H_{15}BrClN_3O_3$ requires C, 44.94; H, 3.74; Br, 19.97; Cl, 8.86; N, 10.48%); ν_{max}(Nujol)/cm^{-1} 3170br (NH), 1740s and 1725s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 3.86 (3 H, s, CO_2Me), 7.57 (5 H, m, ArCH), 8.07 (2 H, t, C_5H_5N), 8.57 (1 H, t, C_5H_5N) and 8.95 (2 H, d, C_5H_5N).

N-[(3-*Benzoylamino*-5-*benzoylhydrazino*-2,5-*dioxo*-1,4-*di*-p-*tolyl*)-3-*azapentyl*]*pyridinium Bromide* **5**·HBr (Ar = *p*-MeC_6H_4, R = COPh).—Hydrazino pyridinium salt **2** (Ar = *p*-MeC_6H_4, R = COPh) (10 mmol) and NEt_3 (2 cm^3) were heated under reflux in acetonitrile (50 cm^3) for 4 h. The precipitate of **5**·HBr (Ar = *p*-MeC_6H_4, R = COPh) was isolated, filtered and washed with acetone and ether. Yield 9%, m.p. >260 °C; ν_{max}/cm^{-1} 3200br (NH), 1714s, 1677s and 1660s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 2.22 (3 H, s, Me), 2.32 (3 H, s, Me), 6.12 (1 H, s, CH), 8.02 (21 H, m, Ar, ArCH and C_5H_5N) and 9.16 (2 H, d, C_5H_5N).

Thermolysis of the Salt **5**·HBr.—The salt **5**·HBr (Ar = *p*-Me_6H_4, R = COPh) and NEt_3 were thermolysed in acetonitrile for 4 h. The hydantoin **6** (Ar = *p*-MeC_6H_4, R = COPh) was obtained and characterized by ^{1}H NMR spectroscopy, and by TLC on silica gel Merck 60 (eluent, ether–light petroleum, 2:1; R_f 0.57).

N,N′-*Diaminohydantoins* **6**.—Hydrazido pyridinium bromide **2** (10 mmol) and NEt_3 (2 cm^3) were heated under reflux in acetonitrile (50 cm^3) for 4 h. After evaporation of acetonitrile (30 cm^3), the residue was diluted with water (100 cm^3) and extracted with dichloromethane. Evaporation of the extract then gave the *N,N′*-diaminohydantoin **6** as a solid which was recrystallized from benzene.

1,3-*Dibenzoylamino*-5-*phenylimidazolidine*-2,4-*dione* **6** (Ar = C_6H_5, R = COPh). Yield 84%, m.p. 178 °C (Found: C, 66.4; H, 4.35; N, 13.6%; M$^+$, 414.133. $C_{23}H_{18}N_4O_4$ requires C, 66.67; H, 4.35; N, 13.53; *M*, 414.1328); ν_{max}(Nujol)/cm^{-1} 3200br (NH), 1805w, 1740s and 1655s (CO); δ_H($CDCl_3$) 5.50 (1 H, s, CH) and 7.40 (15 H, m, Ar).

1,3-*Dibenzoylamino*-5-p-*chlorophenylimidazolidine*-2,4-*dione* **6** (Ar = *p*-ClC_6H_4, R = COPh). Yield 75%, m.p. 182 °C (Found: C, 61.45; H, 3.8; Cl, 7.9; N, 12.35; M$^+$, 448.094. $C_{23}H_{17}ClN_4O_4$ requires C, 61.54; H, 3.79; Cl, 7.91; N, 12.49; *M*$^+$, 448.0938); ν_{max}(Nujol)/cm^{-1} 3220br (NH), 1800w, 1735s and 1665s (CO); δ_H($CDCl_3$) 5.52 (1 H, s, CH), 7.40 (14 H, m, Ar).

1,3-*Dibenzoylamino*-5-p-*tolylimidazolidine*-2,4- *dione* **6** (Ar = *p*-MeC_6H_4, R = COPh). Yield 60%, m.p. 256 °C (Found: C, 67.05; H, 4.6; N, 13.25%, M$^+$, 428.148. $C_{24}H_{20}N_4O_4$ requires C, 67.29; H, 4.67; N, 13.08; *M*, 428.1484); ν_{max}(Nujol)/cm^{-1} 3240br (NH), 1812w, 1752s and 1655s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 2.15 (3 H, s, Me), 5.31 (1 H, s, CH) and 7.40 (14 H, m, Ar).

1,3-*Dimethoxycarbonylamino*-5-*phenylimidazolidine*-2,4-*dione* **6** (Ar = C_6H_5, R = CO_2Me). Yield 55%, m.p. 148 °C (Found: C, 48.15; H, 4.35; N, 17.3; M$^+$, 322.091. $C_{13}H_{14}N_4O_6$ requires C, 48.45; H, 4.35; N, 17.39; *M*, 322.0913); ν_{max}(Nujol)/cm^{-1} 3320br and 3270br (NH), 1810w, 1755s, 1730s and 1710s (CO); δ_H($CDCl_3$) 3.62 (3 H, s, CO_2Me), 3.70 (3 H, s, CO_2Me), 5.25 (1 H, s, CH) and 7.37 (5 H, m, Ar).

5-p-*Chlorophenyl*-1,3-*dimethoxycarbonylaminoimidazolidine*-2,4-*dione* **6** (Ar = *p*-ClC_6H_4, R = CO_2Me). Yield 60%, m.p. 190 °C (Found: C, 43.8; H, 3.7; Cl, 10.00; N, 15.6; M$^+$, 356.051. $C_{13}H_{13}ClN_4O_6$ requires C, 43.76; H, 3.65; Cl, 9.96; N, 15.71; *M*$^+$, 356.0523); ν_{max}(Nujol)/cm^{-1} 3340br and 3260br (NH), 1809w, 1755s, 1743s and 1722s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 3.75 (3 H, s, CO_2Me), 3.82 (3 H, s, CO_2Me), 5.30 (1 H, s, CH) and 7.37 (4 H, m, Ar); δ_C($CDCl_3$ + CF_3CO_2H) 51.4 (q, Me), 54.7 (q, Me), 64.1 (d, CHAr), 154.8 (s, CO), 156.0 (s, CO), 156.5 (s, CO), 167.6 (s, CO), 128.4 (m, Ar), 129.7 (dd, Ar), 129.8 (dt, Ar) and 136.7 (tt, Ar).

1,3-*Dimethoxycarbonylamino*-5-p-*tolylimidazolidine*-2,4-*dione* **6** (Ar = *p*-MeC_6H_4, R = CO_2Me). Yield 75%, m.p. 171 °C (Found: C, 50.05; H, 4.55; N, 16.5%; M$^+$, 336.106. $C_{14}H_{16}N_4O_6$ requires C, 50.00; H, 4.76; N, 16.67; *M*, 336.1069); ν_{max}(Nujol)/cm^{-1} 3320br and 3290br (NH), 1810w, 1757s, 1734s and 1725s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 2.34 (3 H, s, Me), 3.72 (3 H, s, CO_2Me), 3.79 (3 H, s, CO_2Me), 5.26 (1 H, s, CH) and 7.40 (4 H, m, Ar).

N′-*Methoxycarbonyl*-2-*methoxy*-2-p-*tolylacetohydrazide* **8** (Ar = *p*-MeC_6H_4, R = CO_2Me).—Hydrazido pyridinium salt **2** (Ar = *p*-MeC_6H_4, R = CO_2Me) (5 mmol) and NEt_3 (5 mmol) were heated under reflux in methanol (40 cm^3) for 1 h. After evaporation of methanol (30 cm^3), the residue was diluted with water (100 cm^3) and extracted with ether (2 × 50 cm^3). The extract was washed with water (20 cm^3), dried (Na_2SO_4) and then evaporated. The residue was precipitated by addition of ether–light petroleum (1:1). The α-methoxyhydrazide **8** was recrystallized from methanol 60%, m.p. 113 °C;[10] ν_{max}(Nujol)/cm^{-1} 3225br (NH); 1743s and 1661s (CO); δ_H($CDCl_3$ + CF_3CO_2H) 2.40 (3 H, s, Me), 3.37 (3 H, s, OMe), 3.72 (3 H, s, CO_2Me), 4.70 (1 H, s, CH) and 7.20 (4 H, m, Ar).

N,N′-*Diaminohydantoins* **9**.—α-Halogenohydrazide **1** (5 mmol), hydrazido pyridinium salt **2** (5 mmol) and triethylamine

($2\ cm^3$) were refluxed in acetonitrile ($50\ cm^3$) for 4 h. After evaporation of acetonitrile ($30\ cm^3$), the residue was diluted with water ($50\ cm^3$) and acidified with HCl ($4\ mol\ dm^{-3}$) (pH 4–5), then extracted with dichloromethane ($2 \times 50\ cm^3$). The extract was washed with water ($20\ cm^3$), dried (Na_2SO_4) and evaporated. *N,N'*-Diaminohydantoin **9** was obtained as a solid by addition of ether and recrystallized from benzene.

3-Benzoylamino-1-methoxycarbonylamino-5-tolylimidazolidine-2,4-dione **9** (Ar = *p*-MeC_6H_4, R^1 = CO_2Me, R^2 = COPh). Yield 80%, m.p. 172 °C (Found: C, 59.2; H, 4.85; N, 14.15%; M^+, 382.128. $C_{19}H_{18}N_4O_5$ requires C, 59.69; H, 4.71; N, 14.66; *M*, 382.1277); ν_{max}(Nujol)/cm^{-1} 3340br and 3220br (NH), 1811w, 1750s, 1731s and 1650s (CO); δ_H($CDCl_3$) 2.21 (3 H, s, Me), 3.55 (3 H, s, CO_2Me), 5.45 (1 H, s, CH) and 7.36 (9 H, m, Ar).

*3-Benzoylamino-5-*p*-chlorophenyl-1-methoxycarbonylaminoimidazolidine-2,4-dione* **9** (Ar = *p*-ClC_6H_4, R^1 = CO_2Me, R^2 = COPh). Yield 58%, m.p. 161 °C (Found: C, 53.85; H, 3.95; Cl, 8.7; N, 13.5%; M^+, 402.073. $C_{18}H_{15}ClN_4O_5$ requires C, 53.66; H, 3.73; Cl, 8.82; N, 13.91; *M*, 402.0731); ν_{max}(Nujol)/cm^{-1} 3340br and 3215br (NH), 1813w, 1750s, 1730s and 1655s (CO); δ_H($CDCl_3$) 3.60 (3 H, s, CO_2Me), 5.47 (1 H, s, CH) and 7.42 (9 H, m, Ar).

*1-Benzoylamino-5-*p*-chlorophenyl-3-methoxycarbonylaminoimidazolidine-2,4-dione* **9** (Ar = *p*-ClC_6H_4, R^1 = COPh, R^2 = CO_2Me). Yield 50%, m.p. 148 °C (Found: C, 53.4; H, 3.9; Cl, 9.0; N, 13.75%; M^+, 402. $C_{18}H_{15}ClN_4O_5$ requires C, 53.66; H, 3.73; Cl, 8.82; N, 13.91; *M*, 402); ν_{max}(Nujol)/cm^{-1} 3280br and 3220br (NH), 1810w, 1762s, 1717s and 1665s (CO); δ_H($CDCl_3$) 3.62 (3 H, s, CO_2Me), 5.35 (1 H, s, CH) and 7.57 (9 H, m, Ar).

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