Reaction of *N*-Aryl- and *N*-Alkyl-benzimidoyl Chlorides with Silver Nitrate

**Jim Iley,**[*,a] **Emilia Carvalho,**[b] **Fátima Norberto**[b] **and Eduarda Rosa** [*,b]
[a] *POCRG, Chemistry Department, The Open University, Milton Keynes, MK7 6AA, UK*
[b] *CECF, Instituto Nacional de Investigação Científica, Faculdade de Farmácia, Avenida das Forças Armadas, 1699-Lisboa, Portugal*

N-Arylbenzimidoyl chlorides, in which the *N*-aryl group is unsubstituted at the *ortho*- and *para*-positions, react with AgNO$_3$ to yield *N*-(nitroaryl)benzamides in which the NO$_2$ group resides in the *ortho*- or *para*-position. *N*-Arylbenzimidoyl chlorides, in which the *N*-aryl ring is 2,4,6-trisubstituted, react with AgNO$_3$ to yield the corresponding *N*-aryl-*N*-nitrobenzamides. The formation of both types of product can be explained by the intermediacy of an *O*-nitro imidate. Spectroscopic and chemical evidence is presented for the formation of this intermediate in the reaction of *N*-(2,4,6-trisubstituted phenyl)benzimidoyl chlorides with AgNO$_3$. Rearrangement of the *O*-nitro imidate is unimolecular and intramolecular. The rate of rearrangement is independent of the substituent in the *C*-aryl ring, but increases with the electron-withdrawing ability of the substituents in the *N*-aryl ring. A mechanism is proposed in which the imidoyl chloride reacts with AgNO$_3$ to produce first a nitrilium ion which goes on to form an *O*-nitro imidate that subsequently rearranges *via* a homolytic cleavage of the O–NO$_2$ bond. The *ortho:para* ratios of *N*-(nitroaryl)benzamides obtained in the present work indicate that *O*-nitro imidates are not responsible for the high ½*ortho:para* ratios sometimes observed in the nitration of anilides.
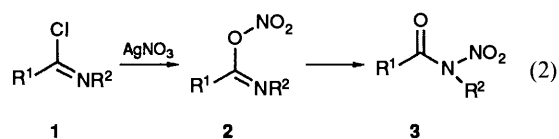
N-Alkylbenzimidoyl chlorides react with AgNO$_3$ to form the corresponding *N*-nitro- and *N*-nitroso-benzamides. The mechanism of formation of the *N*-alkyl-*N*-nitrobenzamide arises from a pathway analogous to that for *N*-aryl-*N*-nitrobenzamides, involving a nitrilium ion that gives rise to an *O*-nitro imidate. The evidence for the formation of the *N*-nitrosobenzamide points to an alternative reaction of the imidoyl chloride with AgNO$_3$. One possible mechanism for this reaction is described.

The rearrangement of imidates to the isomeric amides [eqn. (1)] is a well known reaction.[1] The migrating group, X, can be

$$(1)$$
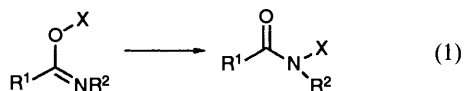
alkyl,[2] aryl,[3] acyl,[4] trialkylsilyl,[5] and even a chlorine atom.[6] For alkyl, aryl and acyl imidates, the rearrangement is irreversible since the amide is the thermodynamically stable isomer. For trialkylsilyl derivatives the reaction is an equilibrium, the imidate form being favoured for substituents R^1, R^2 which lower the π electron density in the amide form. When X is a chlorine atom it appears, from the alkaline hydrolysis of *N*-chloro amides, that the reaction shown in eqn. (1) is reversible. These imidate–amide rearrangements are generally intramolecular, though rearrangements of alkyl imidates can be significantly catalysed by electrophiles[2] and rearrangement of acyl imidates is catalysed by both nucleophiles and electrophiles.[7] The ease of rearrangement appears to depend upon the electrophilic character of the group which migrates and the nucleophilicity of the imidate nitrogen atom,[8] as well as the stereochemistry of the imidate, the *E*-isomer being the only one observed to rearrange.[4]

In continuation of our interest in [1,3] imidate–amide rearrangements,[9] we reasoned that reaction of an imidoyl chloride, **1**, with silver nitrate should provide a simple entry to the analogous *O*-nitro imidates, **2**, and that these would rearrange to *N*-nitro amides, **3** [eqn. (2)]. This expectation was realised,[10] though in our earlier work we were unable to confirm the presence in the reaction of the imidates, **2**. Since *O*-nitro imidates have been invoked to explain high ½*ortho:para* ratios in the nitration of anilides,[11] we have continued our investigations and herein report results that establish *O*-nitro

$$(2)$$

	R^1	R^2
a;	Ph	Ph
b;	4-MeOC$_6$H$_4$	Ph
c;	4-MeC$_6$H$_4$	Ph
d;	4-NO$_2$C$_6$H$_4$	Ph
e;	Ph	4-NO$_2$C$_6$H$_4$
f;	Ph	4-MeOC$_6$H$_4$
g;	Ph	2-MeC$_6$H$_4$
h;	Ph	2-NO$_2$C$_6$H$_4$
i;	Ph	2-CF$_3$C$_6$H$_4$
j;	Ph	2,4-Me$_2$C$_6$H$_3$
k;	Ph	2,4-Cl$_2$C$_6$H$_3$
l;	Ph	2,4-(NO$_2$)$_2$C$_6$H$_3$
m;	Ph	2,6-(NO$_2$)$_2$C$_6$H$_3$
n;	Ph	2,6-Me$_2$C$_6$H$_3$
o;	4-MeOC$_6$H$_4$	2,4-(NO$_2$)$_2$C$_6$H$_3$
p;	Ph	2,4,6-Me$_3$C$_6$H$_2$
q;	4-MeC$_6$H$_4$	2,4,6-Me$_3$C$_6$H$_2$
r;	4-MeOC$_6$H$_4$	2,4,6-Me$_3$C$_6$H$_2$
s;	4-ClC$_6$H$_4$	2,4,6-Me$_3$C$_6$H$_2$
t;	4-CF$_3$C$_6$H$_4$	2,4,6-Me$_3$C$_6$H$_2$
u;	4-NO$_2$C$_6$H$_4$	2,4,6-Me$_3$C$_6$H$_2$
v;	Ph	2,6-Me$_2$-4-Br-C$_6$H$_2$
w;	Ph	2,4,6-Cl$_3$-C$_6$H$_2$
x;	Ph	2,4,6-Bu$^t_3$C$_6$H$_2$
y;	4-NO$_2$C$_6$H$_4$	4-Br-2,6-Me$_2$C$_6$H$_2$

imidates as intermediates and identify the mechanism of the *O*-nitro imidate to *N*-nitro amide rearrangement. Our results show that *O*-nitro imidates cannot be responsible for high ½*ortho:para* ratios for the nitration of anilides. Part of this work has been published as a communication.[12]

Table 1 *N*-Nitroaryl product yields from the reaction of compounds **1a–n** and **7–9** with $AgNO_3$ in CH_3CN

| Substrate | Conc./mol dm^{-3} | T/°C | Percentage yield[a] | | |
			ortho	para	½ortho:para
1a	0.05	22	47.1	45.8	0.51
	0.10	22	45.7 (47.6)	46.7 (46.7)	0.49 (0.51)
	0.125	−10	41.8	41.5	0.52
		5	44.7	40.6	0.55
		22	46.2	46.3	0.50
		36	47.7	44.4	0.53
	0.25	22	46.2	46.3	0.50
	0.5	22	49.3 (45.5)	45.9 (42.3)	0.54 (0.53)
1b	0.125	22	50.1	32.5	0.77
1c	0.125	22	49.1	40.4	0.60
1d	0.125	22	31.6 (25.6)	41.6 (39.6)	0.38 (0.32)
1e			(67)	—	—
1f			(90)	—	—
1g			(32)	(58)	(0.55)[b]
1h			(22)	(45)	(0.49)[b]
1i			(21)	(48)	(0.44)[b]
1j			(67)	—	—
1k			(83)	—	—
1l			(22)	—	—
1m			(17)	—	—
1n			(50)	—	—
7			no reaction		
8			no reaction		
9			(27)	(30)	(0.90)

[a] Measured by multicomponent analysis. Values in parentheses are those calculated from isolated yields. [b] *ortho:para* ratio.

Table 2 ^{1}H NMR data (δ) for imidoyl halides **1l** and **1o**, *O*-acyl imidate **5** and the intermediate formed by reaction of **1l** with $AgNO_3$

| | *C*-Aryl ring | | | *N*-Aryl ring | | |
	C-2	C-3	C-4	C-3	C-5	C-6
1l	←——	7.51–7.67	——→	9.04	8.50	7.22
1l + AgNO₃	←——	7.3–7.7	——→	9.09	8.63	7.85
1o[a]	8.05	7.04	—	8.97	8.42	7.38
5[a]	7.75	6.82	—	8.92	8.31	7.31

[a] Data taken from ref. 8.

Results and Discussion

N-*Arylbenzimidoyl Chlorides*.—The *N*-arylbenzimidoyl chlorides **1a–k** react instantaneously with silver nitrate in acetonitrile solvent. A precipitate of silver chloride is formed and the co-products are the *N*-(nitroaryl)benzamides **4** [eqn. (3)]. The yields of **4** are about 85%, the remainder being the
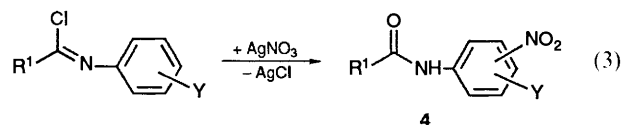
unsubstituted benzanilides arising from competitive hydrolysis of the imidoyl halide by residual water in the solvent. No evidence for the formation of metallic silver was found, nor could we find any spectroscopic evidence for the intermediacy of *O*-nitro imidates **2** or *N*-nitro amides, **3**, even when the *N*-aryl group contains strongly electron-withdrawing substituents. If such intermediates are formed they must readily rearrange to the isomeric *N*-nitroaryl amides. No nitration of R^1 was found. For those substrates that have unblocked *ortho*- and *para*-positions in the *N*-aryl ring, products arising from the rearrangement of the NO_2 group into both positions are found. Table 1 contains data for the relative amounts of the *ortho*- and *para*-isomers formed during the reaction. These clearly show that the product ratio is independent of substrate concentration and temperature. Substituents in the 2-position of the *N*-aryl

ring appear to have little affect on the product ratio. However, for substituents in the 4-position of the *C*-aryl ring groups which are electron donating increase the ½*ortho*:*para* ratio, while electron-withdrawing groups diminish this ratio.

For those substrates that contain a substituent in the 4-position of the *N*-aryl ring, *e.g.* **1e, f, j** and **k**, reaction proceeds similarly with the formation of the corresponding *N*-(2-nitro-4-substituted)arylbenzamides. Also, for those substrates in which both *ortho*-positions carry a substituent, *e.g.* **1n**, reaction proceeds with migration of the NO_2 group to the *para*-position to form *N*-(4-nitro-2,6-disubstituted)arylbenzamides. However, by analogy to the work of Curtin and Miller, we reasoned that introduction of two strongly electron-withdrawing groups into the *N*-aryl ring of the imidoyl chloride, as in **1l, m**, should inhibit the rearrangement of any intermediate *O*-nitro imidate by reducing the electron density of both the imidoyl nitrogen atom and the aryl ring itself. In the event, reaction of either **1l** or **1m** with $AgNO_3$ gave rise to the corresponding *N*-(2,4,6,-trinitrophenyl)benzamide, albeit in low yield. In both reactions, the substituted parent amide, formed by competitive hydrolysis of the imidoyl chloride, accounted for *ca.* 50% of the products,
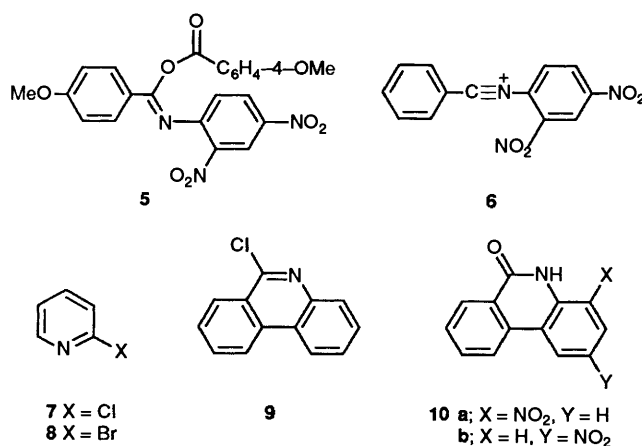

7 X = Cl
8 X = Br

9

10 a; X = NO₂, Y = H
b; X = H, Y = NO₂

Table 3 Partial ^{1}H NMR data (δ) for imidoyl halides **1p**, **1u**, and the corresponding N-nitro amides and intermediates

	2,6-$(CH_3)_2$	4-CH_3	3,5-H
1p	2.02	2.26	6.92
N-nitro amide	2.23	2.29	7.02
intermediate	1.90	1.82	6.65
1u	2.07	2.26	6.94
N-nitro amide	2.23	2.29	7.05
intermediate	1.88	1.81	6.70

Table 4 First-order rate constants for the rearrangement of **2** (formed by reacting **1p–y** with $AgNO_3$) to **3**

Imidoyl halide	T/K	Solvent	$k_1/10^{-3}$ s^{-1} [a]
1p	290	CD_3CN	0.79
	298	CD_3CN	1.69
	298		1.91 [b]
	298		1.81 [c]
	298	$CD_3CN/CDCl_3$ (1:1)	2.20
	298	$CD_3CN/CDCl_3$ (1:3)	2.18
	298	$CD_3CN/CDCl_3$ (1:9)	2.30
	304	CD_3CN	2.35
	315	CD_3CN	8.12
1q	295	CD_3CN	1.75
1r	295	CD_3CN	2.22
1s	295	CD_3CN	1.80
1t	295	CD_3CN	2.00
1u	295	CD_3CN	0.079
	285		0.25
	295		1.09
	305		2.6
	315		11.1
1w	295	CD_3CN	>50
1y	295	CD_3CN	18

[a] [substrate] = 0.15 mol dm^{-3} unless otherwise stated. [b] [substrate] = 0.075 mol dm^{-3}. [c] [substrate] = 0.30 mol dm^{-3}.

the remainder being highly coloured unidentified material. However, monitoring the reaction of **1l** with $AgNO_3$ by ^{1}H NMR spectroscopy revealed the rapid formation of an intermediate that gradually decayed over 48 h to give the observed products. Comparison of our spectroscopic data with those of Curtin and Miller[8] for the formation of the O-acyl imidate **5** from the imidoyl chloride **1o** is given in Table 2. Whereas the ^{1}H chemical shifts of the N-aryl ring in **1o** and **5** are remarkably similar, addition of $AgNO_3$ to **1l** causes a significant low-field shift of ca. δ 0.6 for the proton attached to C-6. Thus, we discount the possibility that the observed intermediate is an O-nitro imidate, and favour the more likely structure **6**, a nitrilium ion, on the basis of the large low-field shift. Further evidence that iminium ions may be intermediates in these reactions comes from results with the cyclic compounds **7–9**. Compounds **7** and **8** do not react with $AgNO_3$, and compound **9** reacts only very slowly (2–3 months). These cyclic substrates are less able to accommodate linear nitrilium ion intermediates. The products from the reaction of compound **9** with $AgNO_3$ are 2- and 4-nitrophenanthridin-6($5H$)-one, **10a** and **b** [and the parent phenanthridin-6($5H$)-one from competitive hydrolysis] in yields of 27% and 30% respectively. The ortho:para ratio of 0.9, is reasonably consistent with the results in Table 1. Significantly, the fixed E-configuration of the imidoyl chloride **9** has no obvious effect on the relative amounts of ortho and para substituted products formed.

Our lack of success in obtaining evidence for O-nitro imidate

and N-nitro amide intermediates in the series **1a–n**, where the N-aryl ring has a free 2- or 4-position, led us to investigate the reaction of silver nitrate with the imidoyl chlorides **1p–y**, in which the 2,4- and 6-positions are blocked. Thus, reaction of **1p** with $AgNO_3$ gave rise to a product that had spectral and analytical data which were consistent with its formulation as the corresponding N-nitro amide, **3p** [eqn. (2)] (see the Experimental). In particular, IR absorptions 1705, 1577 and 1325 cm^{-1} are those expected for an N-nitro amide.[13] Elemental analysis is consistent with the molecular formula, and EI mass spectrometry reveals an $(M + 1)^+$ peak at 285 and $(M - NO)^+$ at 254. The ^{1}H NMR spectrum displays the usual five-proton multiplet for the C-aryl ring, and for the N-aryl ring a six-proton singlet for the two ortho CH_3 groups, a three proton singlet for the para CH_3 group and a two proton singlet for the meta hydrogen atoms. Final structural evidence was obtained from the hydrolysis of the N-nitro amide in 10% aqueous sodium hydroxide solution. After acidification and extractive work-up with CH_2Cl_2, two compounds were isolated in quantitative yield in the ratio 1:3; N-(2,4,6-trimethylphenyl)benzamide and N-nitro-2,4,6-trimethylaniline. The former arises from denitration of the N-nitro amide, and the latter from the normal hydrolysis of an amide. This pattern of reactivity for N-nitro-N-aryl amides has been commented upon previously.[14]

Other imidoyl chlorides **1q–y** behave similarly, the N-nitro amides being isolated in good yields by flash column chromatography. When these reactions were monitored by ^{1}H NMR spectroscopy, an intermediate was detected which rapidly decomposes to the N-nitro amide. As compared with the imidoyl chloride **1** and the N-nitro amide, **3**, this intermediate exhibited characteristic high field shifts in the ^{1}H NMR spectrum of the signals due to both methyl and ring protons of the N-aryl ring. Table 3 presents representative data for two substrates, **1p** and **1u**, that demonstrate this effect, and Fig. 1 illustrates clearly that the progress of the rearrangement may be monitored by ^{1}H NMR spectroscopy. We propose that the intermediate observed in these reactions is the O-nitro imidate, **2**, for the following reasons. First, the shifts to higher field for the ^{1}H NMR signals of the intermediate parallel those observed for the formation of O-acyl imidates by the reaction of imidoyl chlorides with silver benzoates.[8] Second, the intermediate is observed to be a nitrating agent. Thus, addition of N,N-dimethyl-4-toluidine to a reaction mixture involving **1p** results in rapid quantitative nitration of the toluidine and formation of N-(2,4,6-trimethylphenyl)benzamide as the co-product, and no intermediate corresponding to **2** could be detected. Moreover, nitration of N,N-dimethyl-4-toluidine by the N-nitrobenzamide **3p** requires one–two days, whereas nitration by benzoyl nitrate, a compound isostructural with the proposed O-nitro imidate, **2**, and formed by the reaction of benzoyl chloride and $AgNO_3$, was also rapid. Third, addition of water to solutions containing the intermediate result in its hydrolysis to form N-(2,4,6-trimethylphenyl)benzamide.

The rate of the rearrangement of the O-nitro imidates, **2**, to the corresponding N-nitro amides, **3**, was best monitored using the signals for the ring protons at positions 3 and 5 of the N-aryl ring (Table 3 and Fig. 1). Plots of ln $(a - x)/a$ versus t (where a is the total area of the signals for the ring protons (3-H and 5-H) for both the intermediate and the product N-nitro amide, and x is the corresponding area of the product N-nitro amide) are linear up to ca. 90% reaction, and thus first-order rate constants k_1 can be determined. Rate coefficients obtained by this method, which are reproducible to within $\pm$10%, are contained in Table 4. Several observations are worthy of note. First, the reactions are first-order with respect to the imidates, **2**. Second, the observed first-order rate constants are independent of substrate concentration. Third, the temperature dependence of the rate constants for the rearrangements resulting from the reaction of
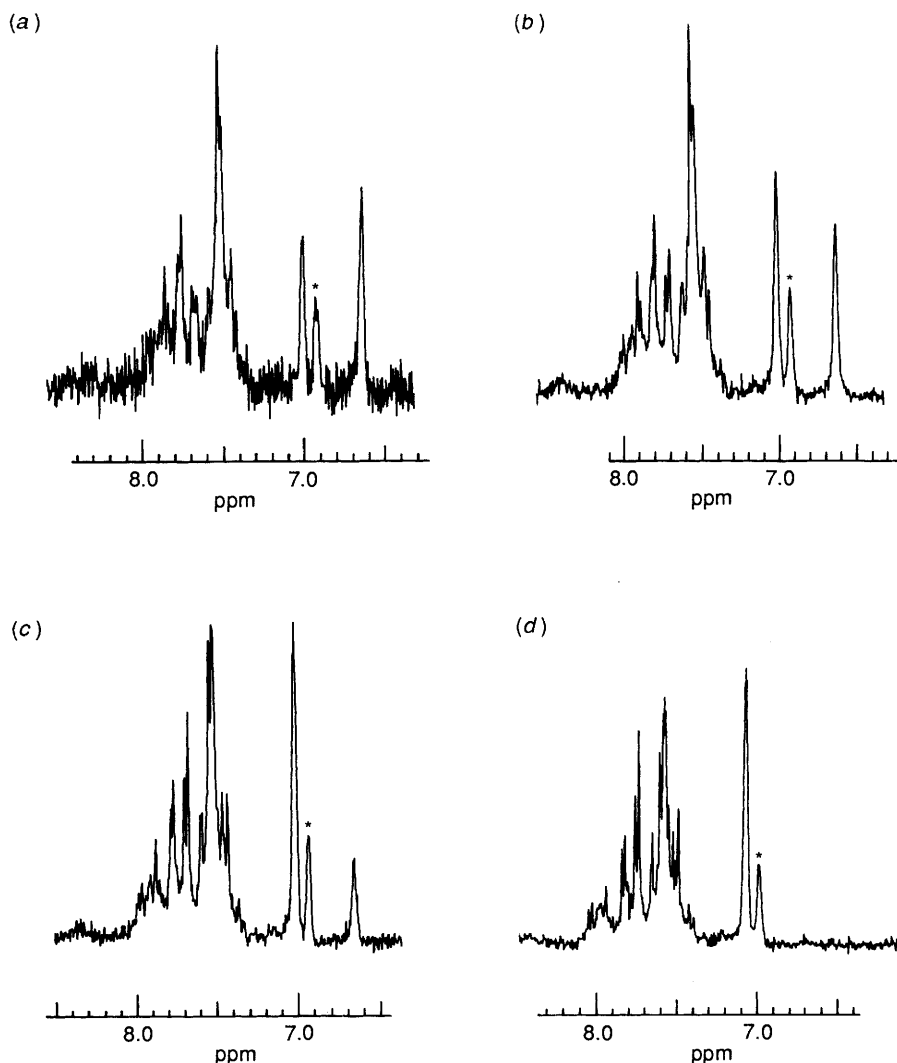
(a)

(b)

(c)

(d)

Fig. 1 The ¹H NMR spectrum of the aromatic region for the reaction of **1p** with $AgNO_3$; (a) 4 min, (b) 7 min, (c) 14 min, (d) 60 min. The peak marked * corresponds to 3-H and 5-H protons of the N-aryl ring of N-(2,4,6-trimethylphenyl)benzamide which arises from hydrolysis of **1p**.

1p and **1u** with $AgNO_3$ give rise to values of E_a = 71 and 89 kJ mol^{-1} and $\Delta S^{\ddagger}$ = (−17 ± 10) and (−2 ± 10) J K^{-1} mol^{-1} respectively. Fourth, the rearrangement is unaffected by varying the solvent polarity. Fifth, the substituent in the C-aryl ring has a negligible effect on the rearrangement rate. Taken together, these observations imply that the rearrangement is unimolecular, and that it is unlikely to involve an ionisation process, such as the formation of NO_2^+ and a benzanilide anion. Indeed, in contrast with the rearrangement of O-acyl imidates[4] and the tautomerism of silyl amides[15] the absence of an effect due to the substituent in the C-aryl ring indicates that the electron density at the imidate nitrogen atom is unimportant to the rearrangement process of O-nitro imidates. This is further borne out by comparison of the data for **1p/1w** and **1u/1y**. Replacing the Me groups in the N-aryl ring by electron-withdrawing substituents increases the rate of rearrangement, rather decreasing it as expected for the ρ value of −0.91 found by Hegarty for the corresponding O-acyl imidates. Both stepwise and concerted mechanisms involving the non-bonding pair electrons on the imidate nitrogen atom are therefore excluded.

On the basis of these observations we propose a mechanism, shown in Scheme 1, for the reaction of N-aryimidoyl chlorides with $AgNO_3$. Initial formation of a nitrilium ion precedes O-nitro imidate formation. This O-nitro intermediate then decomposes via homolytic cleavage of the $O-NO_2$ bond to form
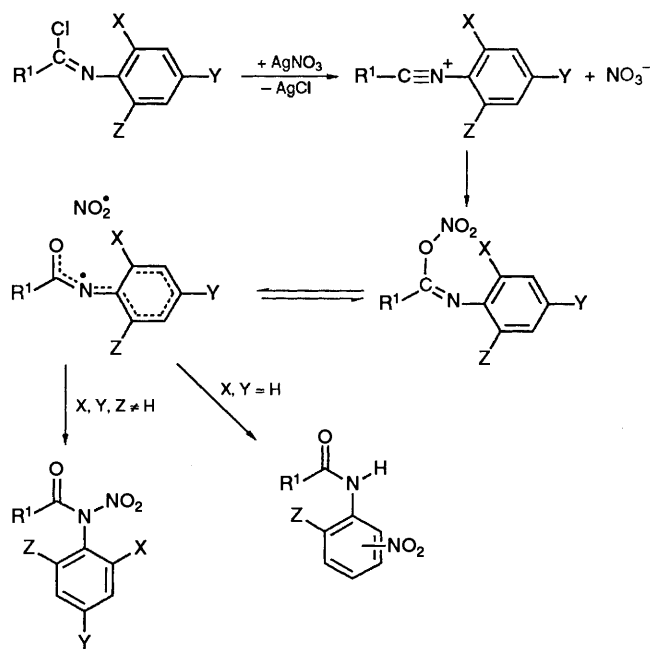
Scheme 1 Pathway for the reaction of N-arylimidoyl chlorides with $AgNO_3$

Table 5 Mass spectral data for the reactions of **1p** and **1t** with $Ag^{15}NO_3$ and $Ag^{14}NO_3$

| Analyte | Relative peak intensity[a] | | | | | | | |
	$m/z = 284$	285	286	287	352	353	354	355
[nitro-14N]-3p	2.7	100	19.8	3.9				
[nitro-15N]-3p	—	—	100	18.1				
[nitro-14N]-3t					8.6	100	16.4	—
[nitro-15N]-3t					—	13.7	100	20.1
Mixture 1[b]	2.3	100	18.5	2.0	5.3	14.0	100	17.6
Mixture 2[c]	—	2.0	100	19.3	4.3	100	21.9	3.4
Reaction 1[d]	2.2	100	20.5	3.0	—	—	100	—
Reaction 2[a]	—	—	100	33.6	—	100	20	—

[a] Most intense peak in the m/z 284–287 and 352–355 regions set to 100 for all samples for comparative purposes. [b] A 1:1 mixture of [nitro-14N]-3p and [nitro-15N]-3t. [c] A 1:1 mixture of [nitro-15N]-3p and [nitro-14N]-3t. [d] A 1:1 mixture of **1p** + $Ag^{14}NO_3$ and **1t** + $Ag^{15}NO_3$. [e] A 1:1 mixture of **1p** + $Ag^{15}NO_3$ and **1t** + $Ag^{14}NO_3$.

a radical pair. Subsequent recombination of this radical pair at the amide nitrogen atom or at the *ortho* and *para* carbon atoms of the *N*-aryl ring yields either an *N*-nitro amide (if X, Y, Z ≠ H) or a ring-substituted *N*-nitroaryl amide (if X or Y = H). Whilst we cannot discount a concerted sigmatropic $[\pi_n + \sigma_2]$ process (n = 2, 4 or 6) as an alternative explanation for the rearrangement, the homolytic mechanism illustrated in Scheme 1 probably accounts better for the formation of ring substituted *para* isomers, especially for compound **9**. It is clear that rearrangement of the NO_2 group into the *N*-aryl ring is much more rapid than to the nitrogen atom, since we did not observe any intermediate in the reactions when X or Y = H. The homolytic mechanism has precedent in the [1,3] carbon-to-carbon rearrangement of an NO_2 in nitroaryl compounds,[16,17] although definitive evidence for this radical mechanism was unforthcoming. Using ^{15}N-labelled $AgNO_3$, and ^{15}N-labelled **1p**, we were unable to observe any chemically induced dynamic nuclear polarization (CIDNP) effects in the ^{15}N NMR spectrum. Nonetheless, the $\frac{1}{2}$*ortho*:*para* ratios observed when substitution of the NO_2 group occurs in the *N*-aryl ring (0.4–0.9) are consistent with both the ratio of unpaired electron density at the *ortho* and *para* carbon atoms in, for example, the anilino radical (0.75)[18] and also the $\frac{1}{2}$*ortho*:*para* value of 0.46 observed for reaction between NO_2 and $PhNH$.[19] Indeed, the spin population in the singly occupied molecular orbital (SOMO) of the benzanilide radical (calculated using the AM1 SCF MO method), which is shown in A, predicts a $\frac{1}{2}$*ortho*:*para* ratio of 0.58.

A
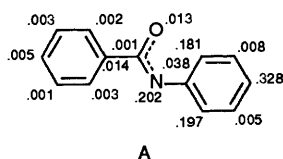
The use of $Ag^{15}NO_3$ did enable the intramolecular nature of the reaction to be revealed, however. Since the *O*-nitro imidates prepared from **1p** and **1t** rearrange at largely similar rates, we reasoned that a mixture of nitro-^{15}N labelled imidate derived from **1p** and nitro-^{14}N labelled imidate derived from **1t** should provide cross-over products if the reaction were intermolecular (Scheme 2). In the event, mass spectral analysis of the resultant products failed to reveal any *N*-nitro amide derived from **1t** that contained a nitro-^{15}N label (Table 5). A further experiment using [15]NO_2 labelled imidate derived from **1t** and nitro-^{14}N labelled imidate derived from **1p** also failed to provide any evidence for cross-over products.

N-*Alkylbenzimidoyl Chlorides.*—We have previously re-
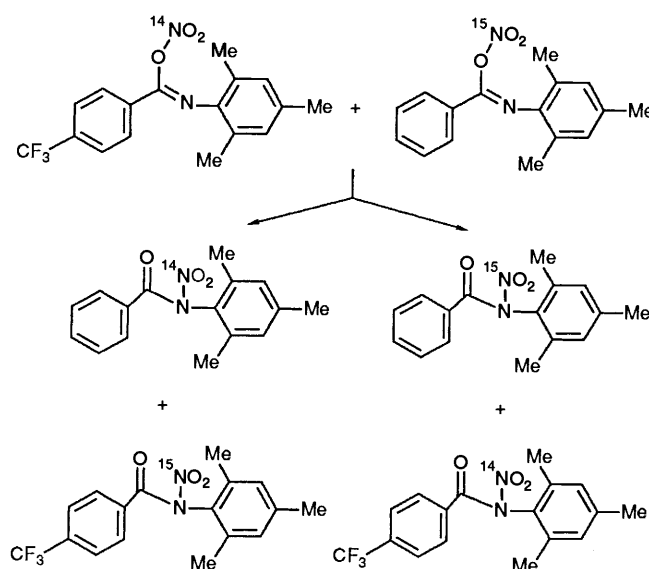
Scheme 2 Potential products from the rearrangement of mixed *O*-nitro imidates

ported that *N*-methylbenzimidoyl chlorides, *e.g.* **11a**, react with $AgNO_3$ to produce the corresponding *N*-nitro amides **12** together with the corresponding *N*-nitroso amides, **13** [eqn. (4)].[10] This is in contradistinction to reactions with *N*-arylbenzimidoyl chlorides (*vide supra*) for which no evidence of the formation of nitrosated products was obtained. The origin of the *N*-nitroso amides is clearly not contamination of the $AgNO_3$, since no nitrite could be determined using a standard method of nitrite analysis.[20] The extent of the formation of these two products is dependent on both the substrate concentration and the temperature at which the reaction is carried out (Table 6). The formation of the *N*-nitro amide is favoured by low temperature and the more dilute solutions. However, the relative amounts of the two compounds appear to be largely independent of the substituent in the *C*-aryl ring.
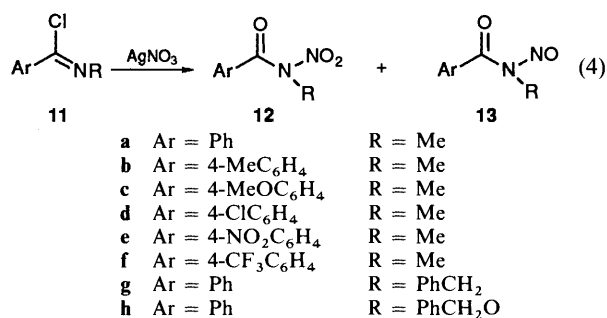
In an attempt to probe this reaction, and in particular to understand the origin of the *N*-nitroso amide, we carried out further series of reactions.

(*a*) The *N*-benzylbenzimidoyl chloride, **11g**, was found to react in an analogous fashion to the *N*-methyl counterparts (Table 6), whereas the *N*-benzyloxybenzimidoyl chloride, **11h**, did not react at all with $AgNO_3$. The unreactivity of **11h** points to the probable involvement of a nitrilium ion in these reactions, as was described above for the *N*-aryl analogues. Johnson and co-workers have also ascribed the low reactivity of *N*-

Table 6 Relative yields of N-nitro- and N-nitroso-amides from the reaction of 11a–h with AgNO₃

Substrate	[Substrate]/mol dm⁻³	T/°C	Yield (%) N-NO₂	N-NO	N-NO₂/N-NO
11a	0.15	−45	93	7	13.4
	0.10	−45	89	11	8.5
		−30	78	22	3.5
		0	76	24	3.1
		25	71	29	2.5
		25	67	33	2[a]
		25	65	35	1.9[b]
		25	64	36	1.7[c]
	0.25	−45	85	15	5.6
		−30	78	22	3.5
		−15	64	36	1.8
		20	64	36	1.8
		48	62	38	1.6
	0.5	−45	81	19	4.4
11b	0.10	−30	68	32	2.1
	0.25	−45	87	13	6.6
11c	0.10	−30	79	21	3.7
		25	50	50	1.0
11d	0.10	−30	71	29	2.5
		25	64	36	1.8
11e	0.10	−30	71	29	2.4
		25	69	31	2.2
11f	0.10	25	73	27	2.7
11g	0.10	25	47	53	0.9
11h	0.10	25	No reaction		—

[a] In CH₃CN–CHCl₃ (2:1). [b] In CH₃CN–CHCl₃ (1:1). [c] In CH₃CN–CHCl₃ (1:2).

$$\underset{\mathbf{11}}{\underset{\text{Ar}}{\overset{\text{Cl}}{\diagdown}}\text{NR}} \xrightarrow{\text{AgNO}_3} \underset{\mathbf{12}}{\underset{\text{Ar}}{\overset{\text{O}}{\diagdown}}\text{N}\diagdown\overset{\text{NO}_2}{\underset{\text{R}}{}}} + \underset{\mathbf{13}}{\underset{\text{Ar}}{\overset{\text{O}}{\diagdown}}\text{N}\diagdown\overset{\text{NO}}{\underset{\text{R}}{}}} \quad (4)$$

a	Ar = Ph	R = Me
b	Ar = 4-MeC₆H₄	R = Me
c	Ar = 4-MeOC₆H₄	R = Me
d	Ar = 4-ClC₆H₄	R = Me
e	Ar = 4-NO₂C₆H₄	R = Me
f	Ar = 4-CF₃C₆H₄	R = Me
g	Ar = Ph	R = PhCH₂
h	Ar = Ph	R = PhCH₂O

alkoxyimidoyl halides to their inability to stabilise a nitrilium ion.[21] Further evidence for the intermediacy of a nitrilium ion comes from the competitive reaction of AgNO₃ and AgNO₂ with 11a, c, e, f. Each of these substrates reacts with AgNO₂ to form the N-nitroso amide as the sole product. In competition reactions using equal amounts of AgNO₃ and AgNO₂, the N-nitro amide product thus arises solely from reaction of AgNO₃ whereas the N-nitroso product arises from reaction of both AgNO₃ and AgNO₂. The product mixtures from such competition reactions may be analysed using eqn. (5) (for the N-nitro product) and eqn. (6) (for the N-nitroso product), where

$$xA = B \qquad (5)$$

$$xC + (1 - x) = D \qquad (6)$$

x is the fraction of the reaction occurring with AgNO₃ and

(1 − x) the fraction occurring with AgNO₂, A the fraction of N-nitro product arising from reaction with AgNO₃ alone, B the fraction of N-nitro product that results from the competition reaction of AgNO₃ and AgNO₂, C the fraction of N-nitroso product arising from reaction with AgNO₃ alone and D the fraction of N-nitroso product that results from competition between AgNO₃ and AgNO₂. The data are contained in Table 7, and these show that AgNO₃ and AgNO₂ have roughly equal selectivity for the imidoyl halides. Since NO₂⁻ is generally some 10⁴–10⁶ times more powerful a nucleophile than NO₃⁻ [22] it follows that the species with which they react is largely unselective, pointing to the involvement of a charged nitrilium ion.

(b) It seems reasonable to consider that the N-alkyl-N-nitro amide 12 is formed via a rearrangement process similar to that described above for the formation of N-aryl-N-nitro amides 3p–y. Therefore, we attempted to intercept the O-nitro imidate intermediate using anisole and N,N-dimethyl-4-toluidine. In the presence of anisole the reaction proceeded normally; no nitration of anisole was observed, and the N-nitro and N-nitroso products were formed in the same amounts as in the absence of anisole. However, the presence of N,N-dimethyl-4-toluidine does influence the outcome of the reaction (Table 8), reducing significantly the amount of N-nitro amide formed. The reduction in N-nitro amide is paralleled by an increase in the formation of the parent amide, the amount of N-nitroso amide remaining largely unaffected. The N,N-dimethyl-4-toluidine itself is nitrated, and the formation of nitrotoluidine and the parent amide is consistent with the presence of an intermediate that is a nitrating agent, such as an O-nitro imidate. Since the N-nitroso amide remains unaffected by the presence of N,N-dimethyl-4-toluidine, it cannot arise from the intermediate that

Table 7 Relative yields of N-nitro- and N-nitroso-amides from the competition reactions of **11a, c, e** and **f** with AgNO$_3$ and AgNO$_2$

Substrate	Fraction from AgNO$_3$ alone		Fraction from AgNO$_2$ alone		Fraction from AgNO$_3$ + AgNO$_2$		
	N-NO$_2$	N-NO	N-NO$_2$	N-NO	N-NO$_2$	N-NO	AgNO$_3$/AgNO$_2$
11a	0.71	0.29	0	1	0.29	0.71	0.41
11c	0.5	0.5	0	1	0.23	0.77	0.46
11e	0.69	0.31	0	1	0.22	0.78	0.32
11f	0.73	0.27	0	1	0.33	0.67	0.45

Table 8 Relative yields of the N-nitro, N-nitroso and parent amide from the reaction of **11a** with AgNO$_3$ in the presence of N,N-dimethyl-4-toluidine[a]

T/°C	[toluidine]/ mol dm^{-3}	Relative yield			N-NO$_2$/N-NO
		N-NO$_2$	N-NO	N-H	
25	0	71	29	0	2.5
	0.01	58	29	13	2.0
	0.05	38	25	37	1.5
	0.1	22	24	54	0.9
−30	0	78	22	0	3.5
	0.01	45	26	29	1.7
	0.05	37	30	33	1.2
	0.1	21	27	52	0.8
−45	0	88	12	0	7.3
	0.02	35	13	52	2.7
	0.05	26	15	59	1.7
	0.1	8	11	81	0.7

[a] Substrate concentration = 0.1 mol dm^{-3}.

forms the N-nitro product. Table 6 demonstrates that neither process is subject to a significant solvent effect.

We also conducted the reaction of **11a** with AgNO$_3$ in the presence of possible electron transfer agents, e.g. 1,4-benzoquinone and 7,7,8,8-tetracyanoquinodimethane (TCNQ), as well as the radical, galvinoxyl. As can be seen from the data in Table 9, none of these affect the outcome of the reaction.

Thus, it would appear that the N-nitro amide arises from the reaction of an N-alkylimidoyl chloride with AgNO$_3$ via the formation of a nitrilium ion, which in turn forms an O-nitro imidate that rearranges to the N-nitro amide probably by the homolytic mechanism described earlier (Scheme 3). The pathway by which the N-nitroso amide is formed in this reaction is
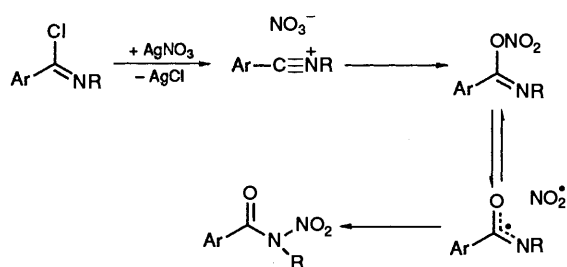
Scheme 3 Mechanism for the formation of N-alkyl-N-nitro amides from the reaction of N-alkylimidoyl chlorides with AgNO$_3$

less obvious, but clearly N-nitroso amide formation cannot diverge from N-nitro amide formation at the O-nitro imidate stage or later (since the presence of the toluidine trap would affect the amount of N-nitroso amide formed). We can therefore conclude that N-nitroso amide formation arises from an alternative pathway that involves the imidoyl chloride or the nitrilium ion. We have some evidence that the pathway for N-nitroso amide formation diverges at the imidoyl halide. Thus,

reaction of N-methylbenzimidoyl bromide gives rise to N-methyl-N-nitrosobenzamide as the sole product (other than the parent amide from concomitant hydrolysis). Since divergence at the nitrilium ion stage would be independent of the halogen atom, we tentatively propose a mechanism for the formation of the N-nitroso amide which involves electron transfer from NO$_3^-$ to the imidoyl halide (Scheme 4). This will generate
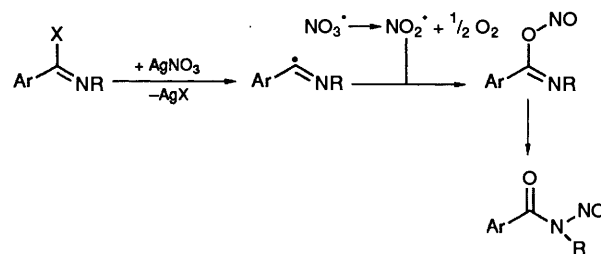
Scheme 4 A possible mechanism for the formation of N-alkyl-N-nitroso amides from the reaction of N-alkylimidoyl halides with AgNO$_3$

initially an imidoyl radical and NO$_3$·, but decomposition of NO$_3$· will generate NO$_2$·. Although the E° value of the NO$_3$·/NO$_3^-$ couple is ca. 2 V,[23] which means that NO$_3^-$ is a poor reductant and NO$_3$· a powerful oxidant, we have been unable to conceive of a satisfactory alternative that is consistent with the experimental observations. The imidoyl radical and NO$_2$· could then combine to form an O-nitroso imidate which is able to rearrange to the N-nitroso amide, in an analogous manner to the O-nitro imidate. Certainly, the intermediacy of an O-nitroso imidate is consistent with this hypothesis as reaction of the imidoyl chloride **11a** with AgNO$_2$ generates the corresponding N-nitroso amide, and the presence of N,N-dimethyltoluidine does not affect the outcome of this reaction. Moreover, there is good evidence that NO$_2$· reacts with neutral substrates via the nitrogen atom, but with radical substrates via the oxygen atom.[24]

Experimental

The benzimidoyl chlorides were synthesized from the parent amide and thionyl chloride, phosphoryl chloride or phosphorus pentachloride using standard procedures.[25] The parent amides were themselves synthesized using the Schotten–Baumann procedure from the appropriate aroyl chloride and amine.[26] N-Methylbenzimidoyl bromide was synthesized from the parent amide using PBr$_5$, and purified by distillation under reduced pressure: b.p. 85 °C, 8 mm Hg; δ_H(CDCl$_3$) 3.7 (3 H, s) and 7.64 (5 H, m).

Silver nitrate was Analar grade, and was dried for 2 h prior to use. Silver nitrite (99%) was purchased from Aldrich, and kept in a desiccator prior to use. Acetonitrile and deuterioacetonitrile were rigorously dried by being refluxed over potassium carbonate followed by distillation onto phosphorus pentaoxide, subsequent redistillation and storage over calcium hydride (acetonitrile) or 4 Å molecular sieves (deuterioacetonitrile).

Reaction of Imidoyl Halides with AgNO$_3$.—(a) *General*

Table 9 Effect of benzoquinone, TCNQ and galvinoxyl on the relative yield of N-nitro- and N-nitroso-amides from the reaction of **11a** with AgNO$_3$

| Added substrate | Conc./mol dm^{-3} | $T/°C$ | [11a]/mol dm^{-3} | Relative yield | | |
				N-NO$_2$	N-NO	N-NO$_2$/N-NO
None		25	0.10	71	29	2.5
		−30	0.10	78	22	3.5
		25	0.25	64	36	1.8
Benzoquinone	1.25	25	0.25	62	38	1.6
TCNQ	0.1	25	0.1	64	36	1.8
	0.1	−30	0.1	79	21	3.8
Galvinoxyl	0.05	25	0.1	75	25	3
	0.10	25	0.1	76	24	3.2

procedure. To a solution of AgNO$_3$ (up to 0.6 mmol) in dry acetonitrile (5 cm^3) at the appropriate temperature was added, with stirring, the imidoyl halide (0.3 mmol) either neat *via* a syringe as a solution in acetonitrile (5 cm^3). Independent experiments revealed that the excess of AgNO$_3$ did not affect the outcome of the reaction. Silver chloride precipitated immediately. The reaction was stirred for a further 10–30 min (this period of time was not critical), the solution then filtered and the solvent evaporated. The products were separated and isolated by column chromatography using silica gel H type 60, the eluent being CH$_2$Cl$_2$ for the substituted N-(nitroaryl)-benzamides, and ether–light petroleum (b.p. 40–60 °C) for the N-nitro and N-nitroso amides.

(*b*) *Kinetic procedure.* The appropriate benzimidoyl chloride, **1p–y** (*ca.* 10^{-4} mol) was dissolved in deuteriated acetonitrile (0.5 cm^3) and placed in an NMR tube. Silver nitrate (1.5 × 10^{-4} mol) was added, the tube inverted to collect the precipitated AgCl in the cap, and the tube transferred to the probe of a JEOL FX90Q spectrometer. Spectra were collected every 20 s for up to 25 min. The spectra were analysed as described in the Results and Discussion section.

Product Analysis.—(*a*) *Identification.* Products isolated from the reactions of imidoyl chlorides with AgNO$_3$ were identified by comparison with authentic materials and by spectroscopic methods. N-Alkyl-N-nitro- and N-alkyl-N-nitroso-benzamide standards were synthesized by previously reported procedures.[10,14] Similarly, the substituted N-(nitroaryl)benzamides were prepared by standard methods,[26] including the phenanthridone derivatives.[27] Compounds that have not been reported heretofore are as follows.

3p: m.p. 72 °C (decomp.); ν_{max}/cm^{-1} 1702, 1577 and 1325; δ_H(CDCN$_3$) 2.23 (6 H, s, N-2,6-CH_3Ar), 2.29 (3 H, s, N-4-CH_3Ar), 7.02 (2 H, s, N-Ar) and 7.39–7.79 (5 H, m, Ph); m/z 285 (M + 1), 254 (M − NO) (Found: C, 68.0; H, 5.9; N, 9.5. Calc. for C$_{16}$H$_{16}$N$_2$O$_3$: C, 67.72; H, 5.63; N, 9.85%).

3q: m.p. 70–74 °C (decomp.); ν_{max}/cm^{-1} 1706, 1570 and 1329; δ_H(CD$_3$CN) 2.22 (6 H, s), 2.29 (3 H, s), 2.38 (3 H, s), 7.01 (2 H, s) and 7.24–7.78 (4 H, AA′BB′, 4 H, m).

3r: oil; ν_{max}/cm^{-1} 1706, 1575 and 1317; δ_H(CD$_3$CN) 2.24 (6 H, s), 2.27 (3 H, s), 3.80 (3 H, s), 6.79–7.67 (AA′BB′) and 6.92 (2 H, s).

3s: m.p. 75–78 °C (decomp.); ν_{max}/cm^{-1} 1695, 1578 and 1327; δ_H(CD$_3$CN) 2.20 (6 H, s), 2.28 (3 H, s), 7.03 (2 H, s) and 7.47–7.79 (4 H, AA′BB′).

3t: ν_{max}/cm^{-1} 1700, 1580 and 1325; δ_H(CD$_3$CN) 2.23 (6 H, s), 2.30 (3 H, s), 7.04 (2 H, s) and 7.72–7.96 (4 H, AA′BB′); m/z 353 (M + 1), 322 (M − NO) (Found: C, 58.1; H, 4.7; N, 7.1. Calc. for C$_{16}$H$_{13}$N$_2$O$_3$: C, 57.98; H, 4.26; N, 7.9%).

3u: m.p. 80–85 °C (decomp.); ν_{max}/cm^{-1} 1705, 1580 and 1340; δ_H(CD$_3$CN) 2.25 (6 H, s), 2.30 (3 H, s), 7.04 (2 H, s) and 7.85–8.30 (4 H, AA′BB′).

3v: m.p. 98–100 °C (decomp.); ν_{max}/cm^{-1} 1710, 1565 and 1320; δ_H(CD$_3$CN) 2.03 (6 H, s), 7.43–7.98 (5 H, m) and 8.23 (2 H, s) (Found: C, 51.6; H, 3.9; N, 7.7. Calc. for C$_{15}$H$_{13}$BrN$_2$O$_3$: C, 51.6; H, 3.75; N, 8.02%).

3w: m.p. 100–102 °C (decomp.); ν_{max}/cm^{-1} 1705, 1595 and 1315; δ_H(CD$_3$CN) 7.42 (2 H, s) and 7.5–8.4 (5 H, m).

3x: ν_{max}/cm^{-1} 1694, 1585 and 1321; δ_H(CD$_3$CN) 1.36 (18 H, s) and 7.4–7.8 (7 H, m) (Found: C, 73.1; H, 8.4; N, 6.9. Calc. for C$_{25}$H$_{34}$N$_2$O$_3$: C, 73.14; H, 8.35; N, 6.82%).

3y: ν_{max}/cm^{-1} 1706, 1575 and 1320; δ_H(CD$_3$CN) 2.27 (6 H, s), 7.44 (2 H, s) and 7.91–8.41 (4 H, AA′BB′).

12g: m.p. 101–103 °C; ν_{max}/cm^{-1} 1700, 1590 and 1320; δ_H(CDCl$_3$) 5.30 (2 H, s) and 7.4 (10 H, m) (Found: C, 65.4; H, 4.6; N, 11.0. Calc. for C$_{14}$H$_{12}$N$_2$O$_3$; C, 65.62; H, 4.69; N, 10.94%).

The product isolated from the alkaline hydrolysis of N-nitro-N-(2,4,6-trimethylphenyl)benzamide was identified as 2,4,6-trimethyl-N-nitroaniline on the basis of the following data: m.p. 111–113 °C; ν_{max}/cm^{-1} 3210, 1590, 1320, 1210 and 860; δ_H(CD$_3$CN) 9.43 (1 H, ex), 2.26 (6 H, s) 2.31 (3 H, s) and 6.96 (2 H, s) (Found: C, 60.1; H, 6.9; N, 15.1. Calc. for C$_9$H$_{12}$N$_2$O$_2$: C, 59.99; H, 6.71; N, 15.05%).

(*b*) *Quantification.* Initially products were quantified by separation and isolation *via* column chromatography followed by a comparison of their individual yields. More commonly, however, for the products derived from N-methyl- and N-benzyl-imidoyl chlorides, yields of individual compounds were determined from the ^{1}H NMR spectrum of the reaction mixture by comparison of the individual peak intensities for the N-Me or N-CH$_2$ signals to the total N-Me or N-CH$_2$ signal intensity for all the products present. Data from the NMR method and from product isolation were reproducible to within ±10%. Product yields from the mixtures derived from N-arylimidoyl chlorides were determined by comparing the UV spectrum of each mixture with those for the standard compounds and carrying out multicomponent analysis.[28] The accuracy of the multicomponent method was tested using standard mixtures of the products that arise from the reaction of **1a** with AgNO$_3$. The results (Table 10) identify the method as appropriate for determining product yields. Comparison of the results obtained for a reaction mixture by the UV method with the yields obtained by product isolation (Table 1) demonstrates that the two methods provide data that are consistent to within ±10%.

Mass Spectral Analysis.—[*Nitro*-^{14}N] and [*nitro*-^{15}N]-**3p** and -**3t** were synthesized from the reactions of **1p** and **1t** with Ag^{14}NO$_3$ and Ag^{15}NO$_3$. Their mass spectra were recorded using a Kratos MS80RFA mass spectrometer. Mixtures of [*nitro*-^{14}N]-**3p** and [*nitro*-^{15}N]-**3t**, and of [*nitro*-^{15}N]-**3p** and [*nitro*-^{14}N]-**3t**, were prepared and subjected to mass spectrometry to verify that exchange of the N-nitro groups did not occur

Table 10 UV multicomponent analysis of standard mixtures of the products that are formed by the reaction of **1a** with $AgNO_3$

	N-(2-nitrophenyl)benzamide (%)		N-(4-nitrophenyl)benzamide (%)		N-phenylbenzamide (%)	
	Present	Determined	Present	Determined	Present	Determined
Mixture 1	40	39.0	40	39.1	20	21.4
Mixture 2	50	50.6	45	45	5	4.3
Mixture 3	35	34.9	35	34.6	30	30.5

between the products. The imidoyl chlorides **1p** and **1t** were then independently reacted with $Ag^{14}NO_3$ and $Ag^{15}NO_3$, respectively, and the two solutions rapidly mixed. After 30 min, the final reaction solutions were subjected to mass spectral analysis. In a similar experiment, the imidoyl halides **1p** and **1t** were reacted with $Ag^{15}NO_3$ and $Ag^{14}NO_3$, respectively, the solutions mixed, and after 30 min analysed by mass spectrometry.

Molecular Orbital Calculations.—The UHF molecular orbital calculations were carried out using the AM1 SCF MO package within MOPAC 4.0,[29] and were performed on a VAX cluster. Complete geometry optimisation was achieved using the Broyden–Fletcher–Goldfarb–Shanno formulation.[30]

References
1 B. C. Challis and J. A. Challis, in *The Chemistry of Amides,* ed. J. Zabicky, Wiley, London, 1970, ch. 13.
2 B. C. Challis and A. D. Frenkel, *J. Chem. Soc., Perkin Trans. 2,* 1977, 1085.
3 K. B. Wiberg and B. I. Rowland, *J. Am. Chem. Soc.,* 1955, **77**, 2205.
4 D. G. McCarthy and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2,* 1977, 1085.
5 A. G. Brook and A. R. Bassindale, in *Rearrangements in Ground and Excited States,* vol. 2, ed. P. de Mayo, Academic, New York, 1980, ch. 9.
6 F. E. Hardy and P. Robson, *J. Chem. Soc. B,* 1967, 1151.
7 B. C. Challis, J. A. Challis and I. R. McDermott, *J. Chem. Soc., Perkin Trans. 2,* 1979, 634.
8 D. Y. Curtin and L. L. Miller, *J. Am. Chem. Soc.,* 1967, **89**, 637.
9 B. C. Challis, J. A. Challis and J. N. Iley, *J. Chem. Soc., Perkin Trans. 2,* 1978, 813; B. C. Challis, J. N. Iley and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2,* 1983, 1037; J. N. Iley, A. R. Bassindale and P. Patel,

J. Chem. Soc., Perkin Trans. 2, 1984, 77; B. C. Challis and J. N. Iley, *J. Chem. Soc., Perkin Trans. 2,* 1985, 699.
10 E. Carvalho, F. Norberto, E. Rosa, J. N. Iley and P. Patel, *J. Chem. Res., (S),* 1985, 132.
11 See R. B. Moodie, P. N. Thomas and K. Schofield, *J. Chem. Soc., Perkin Trans. 2,* 1977, 1693 and references therein.
12 E. Carvalho, J. N. Iley and E. Rosa, *J. Chem. Soc., Chem. Commun.,* 1988, 1249.
13 R. Campbell and C. J. Peterson, *J. Org. Chem.,* 1963, **28**, 2294.
14 E. Carvalho, J. N. Iley, F. Norberto and E. Rosa, *J. Chem. Res. (S),* 1989, 260.
15 M. Fukui, K. Itoh and Y. Ishii, *J. Chem. Soc., Perkin Trans. 2,* 1972, 1043.
16 P. Helsby and J. Ridd, *J. Chem. Soc., Perkin Trans. 2,* 1983, 1191.
17 C. Bloomfield, A. K. Manglik, R. B. Moodie, K. Schofield and G. D. Tobin, *J. Chem. Soc., Perkin Trans. 2,* 1983, 75.
18 P. Neta and R. W. Fessenden, *J. Phys. Chem.,* 1974, **78**, 523.
19 E. H. Crowston, Ph.D. Thesis, Imperial College, London, 1986.
20 M. C. Rand, A. Greenberg and M. Taras, *Standard Methods for the Examination of Water and Wastewater,* APHA-AWWA-WPCF, 14th edn., Washington, 1975.
21 J. E. Johnson and S. C. Cornell, *J. Org. Chem.,* 1980, **45**, 4144.
22 N. S. Isaacs, *Physical Organic Chemistry,* Longman, Harlow, 1987, ch. 6.
23 E. Baciocchi, T. Del Giacco, S. M. Murgia and G. V. Sebastiani, *J. Chem. Soc., Chem. Commun.,* 1987, 1246.
24 D. K. Bryant, Ph.D. Thesis, University of London, 1989.
25 H. Ulrich, *The Chemistry of Imidoyl Halides,* Plenum, New York, 1968; A. F. Hegarty, J. D. Cronin and F. L. Scott, *J. Chem. Soc., Perkin Trans. 2,* 1975, 429; J. E. Johnson, A. Ghafouripour and Y. K. Haug, *J. Org. Chem.,* 1985, **50**, 993; C. L. Arcus, M. M. Coombs and J. V. Evans, *J. Chem. Soc.,* 1956, 1498; G. M. Badger, J. H. Seidler and B. Thomson, *J. Chem. Soc.,* 1951, 3207.
26 *Vogel's Textbook of Practical Organic Chemistry,* 4th edn., Longman, London, 1978.
27 F. J. Moore and E. H. Huntress, *J. Am. Chem. Soc.,* 1972, **49**, 1324; A. J. Nunn, K. Schofield and R. S. Theobald, *J. Chem. Soc.,* 1952, 2797.
28 J. C. Sternberg, H. S. Stillo and R. H. Schwendeman, *Anal. Chem.,* 1960, **32**, 84.
29 MOPAC 4.0, *Quantum Chemistry Program Exchange,* Program No. 455, Indiana University, 1987.
30 J. J. P. Stewart, in MOPAC Version 4.0, Update to QCPE 455, Indiana University, 1987.