Rearrangement of Imidoyl Nitrates to *N*-Nitro Amides: an Intramolecular [1,3] O-to-N Migration of a Nitro Group

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Imidoyl nitrates, formed by the reaction of imidoyl chlorides with $AgNO_3$, rearrange *via* a unimolecular, intramolecular mechanism probably involving homolytic fission of the O–N bond to yield *N*-nitro amides; migration of the nitro group in *N*-arylimidoyl nitrates to the *ortho*- and *para*-positions of the *N*-aryl ring does not involve a special *ortho*-directing effect.

The rearrangement of imidates to the isomeric amides when the migrating group is alkyl,[1] aryl,[2] or acyl[3] is well known. The reactions are intramolecular, and the ease of rearrangement appears to be related to the electrophilic character of the group which migrates. The [1,3] migration of other groups has been reported only for silylated derivatives, but the mechanism of the tautomerism between *O*-silyl imidate and *N*-silyl amide is not understood.[4] Recently, we reported that the reaction of imidoyl chlorides (**1**) with $AgNO_3$ gave the *N*-nitro amides (**3**).[5] We now present results which show this reaction to involve a [1,3] O-to-N rearrangement of an NO_2 group, converting the imidate (**2**) into the amide (**3**). These results are of relevance to the nitration of anilides (R^2 = aryl), for which high $\frac{1}{2}o:p$ ratios have been attributed to the formation of imidoyl nitrate intermediates such as (**2**).[6]

Addition of $AgNO_3$ to (**1a**) in acetonitrile yields the *N*-nitro amide (**3a**), whereas the same reaction involving the *N*-phenylimidoyl chloride (**1k**) gives a mixture of 2- and 4-nitro-substituted benzanilides. In neither case is an intermediate observed by ^1H n.m.r. spectroscopy, and the migration of the NO_2 group to the ring is not inhibited even for (**1p**). However, when the 2-, 4-, and 6-positions in the *N*-phenyl ring of (**1**) are blocked, *e.g.* in (**1b**—**j**), the reaction proceeds as for (**1a**) to give 85—90% yields of the corresponding *N*-nitro *N*-aryl amides (**3b**—**j**).

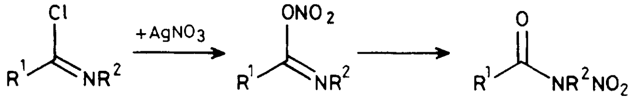
^1H N.m.r. spectroscopy indicates the presence of an intermediate in these reactions which gradually decomposes to the *N*-nitro amide. The ^1H n.m.r. spectrum of this intermediate shows characteristic upfield shifts, as compared with (**1**) and (**3**), of signals due to both methyl and ring protons of the *N*-aryl group. This is indicative of an imidate intermediate (**2**).[7] Other evidence that the intermediate has structure (**2**) comes from the addition of *N*,*N*-dimethyltoluidine to the reaction; no intermediate is observed and no *N*-nitro amide is produced. However, the toluidine is quantitatively nitrated in a similar manner to that observed when benzoyl nitrate ($PhCO_2NO_2$) is used, and the amide co-product is *N*-(2,4,6-trimethylphenyl)benzamide.

The rate at which the imidoyl nitrate (**2**) rearranges to the *N*-nitro amide (**3**) can be monitored by using the ^1H n.m.r. signal for the two aromatic protons of the *N*-aryl ring. Reactions are first-order in (**2**) and the rate constants are

Table 1. First-order rate constants for the rearrangement of (**2**) to (**3**).

Compd.	T/K	Solvent	$10^3 k_1$/s^{-1}
(**2b**)	298	CD_3CN	1.91[a]
		CD_3CN	1.69[b]
		CD_3CN	1.81[c]
		$CD_3CN/CDCl_3$ (1 : 1)	2.20
		$CD_3CN/CDCl_3$ (1 : 3)	2.18
		$CD_3CN/CDCl_3$ (1 : 9)	2.30
(**2c**)	295	CD_3CN	1.75
(**2d**)	295	CD_3CN	2.22
(**2e**)	295	CD_3CN	1.80
(**2f**)	295	CD_3CN	2.00
(**2g**)	275	CD_3CN	0.079
	285	CD_3CN	0.25
	295	CD_3CN	1.09
	305	CD_3CN	2.6
	315	CD_3CN	11.1
(**2i**)	295	CD_3CN	18
(**2j**)	295	CD_3CN	>50

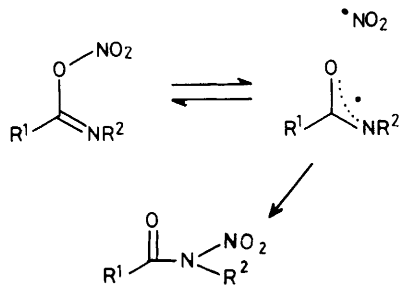
[a] [(**2b**)] = 0.075 mol l^{-1}. [b] [(**2b**)] = 0.15 mol l^{-1}. [c] [(**2b**)] = 0.30 mol l^{-1}.



(**1**) (**2**) (**3**)

	R^1	R^2
a;	Ph	Me
b;	Ph	2,4,6-$Me_3C_6H_2$
c;	4-MeC_6H_4	2,4,6-$Me_3C_6H_2$
d;	4-$MeOC_6H_4$	2,4,6-$Me_3C_6H_2$
e;	4-ClC_6H_4	2,4,6-$Me_3C_6H_2$
f;	4-$CF_3C_6H_4$	2,4,6-$Me_3C_6H_2$
g;	4-$NO_2C_6H_4$	2,4,6-$Me_3C_6H_2$
h;	Ph	4-Br-2,6-$Me_2C_6H_2$
i;	4-$NO_2C_6H_4$	4-Br-2,6-$Me_2C_6H_2$
j;	Ph	2,4,6-$Cl_3C_6H_2$
k;	Ph	Ph
l;	4-$NO_2C_6H_4$	Ph
m;	4-MeC_6H_4	Ph
n;	Ph	2-$CF_3C_6H_4$
o;	Ph	2-$NO_2C_6H_4$
p;	Ph	2,4-$(NO_2)_2C_6H_3$

contained in Table 1. These are independent of substrate concentration, and the $\Delta S^‡$ value calculated for (**2g**) is 0($\pm$5) J K^{-1} mol^{-1}. It follows that the reaction is unimolecular. There appears to be little solvent effect on the reaction, which implies that it does not involve an ionisation process, *e.g.* to form NO_2^+ and a benzanilide anion. Consistent with this is the almost negligible effect on the rate of the substituent in R^1. Formation of a benzanilide anion ought to exhibit a similar Hammett substituent effect as the ionisation of benzoic acids. The lack of such an effect also indicates that electron density at the imidate N atom is not involved in the rate-limiting process. This is in contradistinction to the rearrangement of acyl imidates,[3] and the tautomerism of silyl amides.[8] Moreover, replacing a 4-Me group in the *N*-aryl ring by 4-Br increases the rate, in contrast to the decrease expected from the ρ value of −0.91 calculated by Hegarty for the rearrangement of acyl imidates.[3] Thus, both stepwise and concerted mechanisms involving the non-bonding pair of electrons on the imidate N atom are excluded. Though we cannot discount that the rearrangement proceeds by a concerted sigmatropic [$\pi_2 + \sigma_2$] process, by analogy to the [1,3] carbon-to-carbon rearrangement of an NO_2 group in nitroaryl compounds,[9,10] we believe that the data point to a rate-limiting homolytic cleavage of the imidate O–N bond followed by a recombination at the amide N atom of the radical pair thus formed (Scheme 1).



Scheme 1. Mechanism of the rearrangement of imidoyl nitrates to nitro amides.

A mass spectrometric study of the rearrangement of [*nitro*-^{15}N]-(**2b**) [prepared from (**1b**) and $Ag^{15}NO_3$] in the presence of [*nitro*-^{14}N]-(**2f**) showed that only [*nitro*-^{15}N]-(**3b**) and [*nitro*-^{14}N]-(**3f**) were produced. Likewise, [*nitro*-^{14}N]-(**2b**) and [*nitro*-^{15}N]-(**2f**) produce only [*nitro*-^{14}N]-(**3b**) and [*nitro*-^{15}N]-(**3f**). Since (**2b**) and (**2f**) rearrange at similar rates, the rearrangement must be intramolecular.

Reaction of imidoyl chlorides (**1 k**—**o**) yields 4- and 6-nitroarylbenzamides in *o* : *p* ratios between 0.44 for (**1n**) and (after statistical correction) 0.52 for (**1k**). These ratios are independent of concentration and temperature, which implies that the reactions are also intramolecular. Clearly no special *ortho*-directing effect is exhibited by the imidoyl nitrate intermediate (**2**). Indeed, the imidoyl nitrate formed from 6-chlorophenanthridine and $AgNO_3$, which is fixed in the *E*-configuration and unable to exhibit an *ortho*-directing effect, forms the corresponding 1- and 3-nitrophenanthridones in a 1-NO_2 : 3-NO_2 ratio of 0.89. Thus, *O*-nitro imidates cannot be responsible for the high ½*o* : *p* ratios (*ca.* 2) observed in the nitration of anilides by acetyl nitrate. The mechanism outlined in Scheme 1 is consistent with the migration of the NO_2 group to the 2- and 4-positions. The *o* : *p* ratios observed in the present work probably reflect the difference in electron density at the 4- and 6-positions in the compounds studied, and, significantly, are consistent with the ½*o* : *p* values of 0.46 and 0.41—1.0 observed for the reactions between $NO_2^•$ and $PhNH^•$ and $PhO^•$, respectively.[11]

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