

## 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<sub>3</sub>, 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,<sup>1</sup> aryl,<sup>2</sup> or acyl<sup>3</sup> 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.<sup>4</sup> Recently, we reported that the reaction of imidoyl chlorides (**1**) with AgNO<sub>3</sub> gave the *N*-nitro amides (**3**).<sup>5</sup> We now present results which show this reaction to involve a [1,3] O-to-N rearrangement of an NO<sub>2</sub> group, converting the imidate (**2**) into the amide (**3**). These results are of relevance to the nitration of anilides (R<sup>2</sup> = aryl), for which high *o*:*p* ratios have been attributed to the formation of imidoyl nitrate intermediates such as (**2**).<sup>6</sup>

Addition of AgNO<sub>3</sub> 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 <sup>1</sup>H n.m.r. spectroscopy, and the migration of the NO<sub>2</sub> 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**).

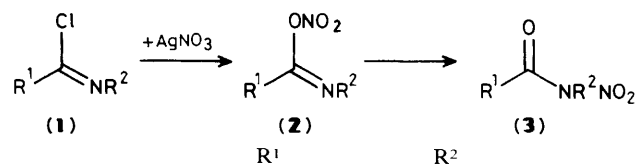
<sup>1</sup>H N.m.r. spectroscopy indicates the presence of an intermediate in these reactions which gradually decomposes to the *N*-nitro amide. The <sup>1</sup>H n.m.r. spectrum of this intermediate shows characteristic upfield shifts, as compared with (**1**) and (**3**), of signals due to both methyl and ring protons of the *N*-aryl group. This is indicative of an imidate intermediate (**2**).<sup>7</sup> 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<sub>2</sub>NO<sub>2</sub>) 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 <sup>1</sup>H 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).

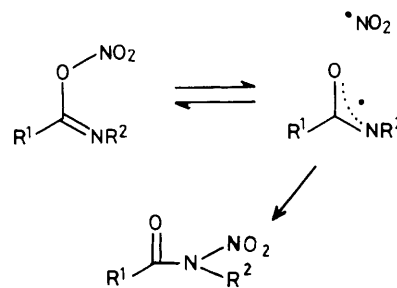
| Compd. | T/K | Solvent                                    | $10^3 k_1/s^{-1}$ |
|--------|-----|--|-------------------|
| (2b)   | 298 | CD <sub>3</sub> CN                         | 1.91 <sup>a</sup> |
|        |     | CD <sub>3</sub> CN                         | 1.69 <sup>b</sup> |
|        |    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

<sup>a</sup> [(2b)] = 0.075 mol l<sup>-1</sup>. <sup>b</sup> [(2b)] = 0.15 mol l<sup>-1</sup>. <sup>c</sup> [(2b)] = 0.30 mol l<sup>-1</sup>.



|    |   |   |
|----|---|---|
| a; | Ph  | Me  |
| b; | Ph  | 2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>               |
| c; | 4-MeC <sub>6</sub> H <sub>4</sub>               | 2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>               |
| d; | 4-MeOC <sub>6</sub> H <sub>4</sub>              | 2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>               |
| e; | 4-ClC <sub>6</sub> H <sub>4</sub>               | 2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>               |
| f; | 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> | 2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>               |
| g; | 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> | 2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>               |
| h; | Ph  | 4-Br-2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>2</sub>            |
| i; | 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> | 4-Br-2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>2</sub>            |
| j; | Ph  | 2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub>               |
| k; | Ph  | Ph  |
| l; | 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> | Ph  |
| m; | 4-MeC <sub>6</sub> H <sub>4</sub>               | Ph  |
| n; | Ph  | 2-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>                   |
| o; | Ph  | 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>                   |
| p; | Ph  | 2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> |

contained in Table 1. These are independent of substrate concentration, and the  $\Delta S^\ddagger$  value calculated for (2g) is  $0(\pm 5)$  J K<sup>-1</sup> mol<sup>-1</sup>. 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<sub>2</sub><sup>+</sup> and a benzanilide anion. Consistent with this is the almost negligible effect on the rate of the substituent in R<sup>1</sup>. 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,<sup>3</sup> and the tautomerism of silyl amides.<sup>8</sup> 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  $\rho$  value of -0.91 calculated by Hegarty for the rearrangement of acyl imidates.<sup>3</sup> 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<sub>2</sub> group in nitroaryl compounds,<sup>9,10</sup> we believe

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

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).

A mass spectrometric study of the rearrangement of [*nitro*-<sup>15</sup>N]- (2b) [prepared from (1b) and Ag<sup>15</sup>NO<sub>3</sub>] in the presence of [*nitro*-<sup>14</sup>N]- (2f) showed that only [*nitro*-<sup>15</sup>N]- (3b) and [*nitro*-<sup>14</sup>N]- (3f) were produced. Likewise, [*nitro*-<sup>14</sup>N]- (2b) and [*nitro*-<sup>15</sup>N]- (2f) produce only [*nitro*-<sup>14</sup>N]- (3b) and [*nitro*-<sup>15</sup>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<sub>3</sub>, 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<sub>2</sub>:3-NO<sub>2</sub> ratio of 0.89. Thus, *O*-nitro imidates cannot be responsible for the high  $\frac{1}{2}o:p$  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<sub>2</sub> 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  $\frac{1}{2}o:p$  values of 0.46 and 0.41—1.0 observed for the reactions between NO<sub>2</sub><sup>•</sup> and PhNH<sup>•</sup> and PhO<sup>•</sup>, respectively.<sup>11</sup>

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