Reaction of *N*-Unsubstituted Imidazoles with Benzonitrile Oxide

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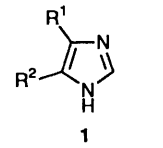
The behaviour of *N*-unsubstituted imidazoles **1** with benzonitrile oxide is reported. The results indicate that in solution a ring-chain tautomerism exists between the cycloadduct **3B** and the *Z*-oxime **3A**; while in the solid state only the chain form **3A** was observed. Oximes of *N*-benzoylimidazol-2-ones **4**, derived from subsequent attack of the 1,3-dipole on both tautomers, and 3,6-diphenyl-1,4,2,5-dioxadiazine **2**, an unusual dimer of the benzonitrile oxide, were also isolated. A mechanism involving a zwitterionic intermediate is proposed. The structure of the oximes of *N*-benzoylimidazol-2-one **4** and **10**, derived from benzonitrile oxide and *p*-toluonitrile oxide respectively, was determined by X-ray diffraction analysis.

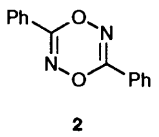
The reaction of tautomerizable isoxazol-5-ones with benzonitrile oxide (BNO) can, under appropriate conditions, lead to products both of expansion and rearrangement of the five-membered ring, namely, to 1,3-oxazin-6-ones[1] and to 2-phenylimidazoles,[2] respectively. The latter, just like other *N*-unsubstituted imidazoles, rather than functioning merely as catalysts for the dimerisation of BNO to 3,6-diphenyl-1,4,2,5-dioxadiazine **2**,[3] quite surprisingly reacted with the dipole, resulting, according to their symmetry, in either a mixture of two isomeric products or one alone. We have described these as cycloadducts **B**.[4]

More recently,[5] during investigations into the behaviour of aromatic azoles with BNO, the reaction with imidazole **1a** was found to lead to the stereospecific formation[6] of the *Z*-oxime **3Aa** by nucleophilic addition to the dipole, excluding the formation of the fused heterocycle **3Ba** by cycloaddition. This conclusion, nevertheless, fails to take into consideration the possibility that, the reaction mechanism aside, the product from nitrile oxide and imidazole might be involved in a tautomeric equilibrium, and that both open form **3A** and closed form **3B** might, therefore, exist. This hypothesis is suggested by chemical evidence and seems consistent, both in terms of ease[7] of the ring-closure of oxime **3A** and by analogy with the reactions of other heteroaromatic compounds with nitrile oxides, such as cycloaddition to 3-pyrrolidinothiophene.[8]

We therefore thoroughly reinvestigated the reaction of imidazoles with BNO and, while all the attempts with the instruments at our disposal to highlight the equilibrium A $\rightleftharpoons$ B [eqn. (1)] failed, we did obtain results which make it possible to define a reasonable reaction mechanism. We were able to show unambiguously the formation of the closed-form **3B** in solution, whereas in the solid state only the structure **3A** is observed and this is confirmed by X-ray studies.[9]



1



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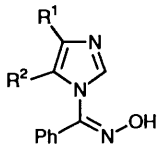
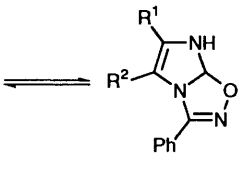
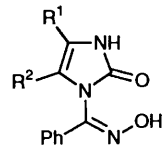


3A



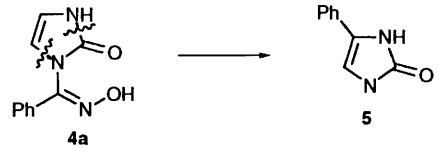
3B

(1)



4

a $R^1 = R^2 = H$
b $R^1 = Me$, $R^2 = H$
c $R^1 = H$, $R^2 = Me$
d $R^1 = Ph$, $R^2 = H$
e $R^1 = H$, $R^2 = Ph$



4a **5**

Scheme 1

Results and Discussion

Reaction of the imidazole **1a** and BNO, under previously reported[5] conditions gave, after careful separation of the products, the dioxadiazine **2**[10] and small quantities of compound **4a**, characterized as the oxime of the *N*-benzoylimidazol-2-one, in addition to the already described[4,5] **3a** and diphenylfuroxan. The structure of compound **4a** has been assigned on the basis of analytical and spectroscopic results (Experimental section) and confirmed by acid hydrolysis[11] of the compound to 3-phenyl-1,2,4-oxadiazolin-5(4*H*)-one **5** (Scheme 1).

The yield of **4a** increased with the increase in the ratio of BNO to imidazole. Its formation, therefore, must be the result of a further attack of BNO on the first product of the reaction, that is to say either on *N*-benzoyl oxime **3A** or on its ring-tautomer **3B** or both. In fact, direct treatment of **3a** with BNO, both generated *in situ* from benzohydroxamoyl chloride and triethylamine and prepared separately,[12] led to quantitative transformation into the imidazolone **4a**.

An identical reaction with BNO occurred using the asymmetric imidazoles **1b–e** ($R^1 \neq R^2$) but, in addition to the expected products **2** and **3**, only one of the two possible isomeric imidazolones **4** was formed in small quantity. In particular, from **1b** and **1c** we derived **4c** and from **1d** and **1e** we derived **4e**.

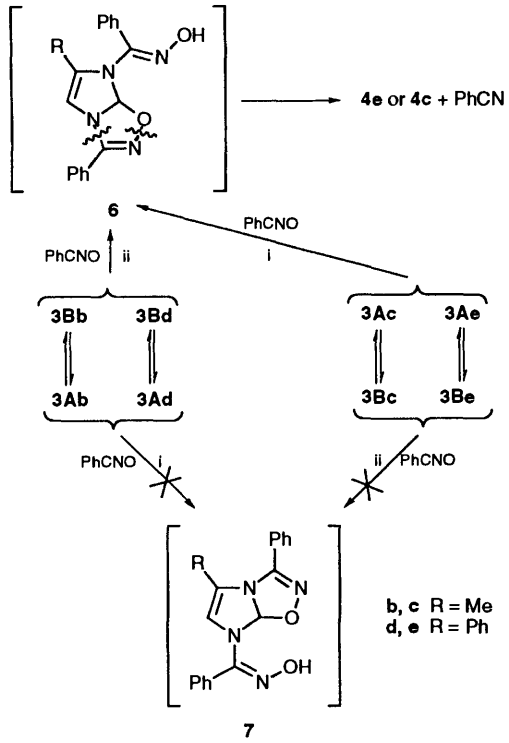
This was confirmed by the direct treatment of the products **3** with BNO (Table 1); **3b** and **3c** produced quantitatively benzonitrile and **4c**; **3d** and **3e** produced quantitatively benzonitrile

Table 1 Products from 3 and BNO or TNO

Compound	Dipole	Product	M.p. (°C)
3a	BNO	**4a**	219
3a	TNO	**4a·10a**	207
3b	BNO	**4c**	250
3b	TNO	**10b**	210
3c	BNO	**4c**	250
3c	TNO	**4c**	250
3d	BNO	**4e**	230
3d	TNO	**10d**	218
3e	BNO	**4e**	230
3e	TNO	**4e**	230

and **4e**. In none of these cases was 3,6-diphenyl-1,4,2,5-dioxadiazine **2** ever isolated. The structures of products **4c** and **4e** were assigned on the basis of analytical and spectroscopic data (Experimental section) and confirmed by analogy to the X-ray structure of product **4a**.

Consistent with the known cleavage of the 1,2,4-oxadiazoline ring,[13] the formation of the imidazolones **4** must require the intermediacy of an imidazooxadiazoline cycloadduct. Since for each pair of isomers **3** only one of the two possible imidazolones **4** was ever isolated, the invoked cycloadduct must be the same in each case. This important consideration suggests that the unisolated oxime of *N*-benzoylimidazooxadiazoline **6** is the key intermediate which leads to the formation of the products of our reaction (Scheme 2). In cases **c** and **e**, the product is formed *via* the open-form **3A**, by cycloaddition to the BNO of the imidazole C=N bond (path i); and in cases **b** and **d**, *via* the closed-form **3B**, by nucleophilic addition to the BNO of the NH group (path ii). The other possible intermediate, the imidazo-oxadiazoline **7**, can be excluded on the basis of the products obtained. Cycloaddition between the imidazole C=N and a nitrile oxide has, to our knowledge, never been observed when the carbon atom α to the nitrogen atom of the C=N is substituted. For example, 4,5-diphenylimidazole and BNO did not give the corresponding imidazolone **4**.[14] Our findings are consistent with those obtained with the 2-picoline and BNO.[15]



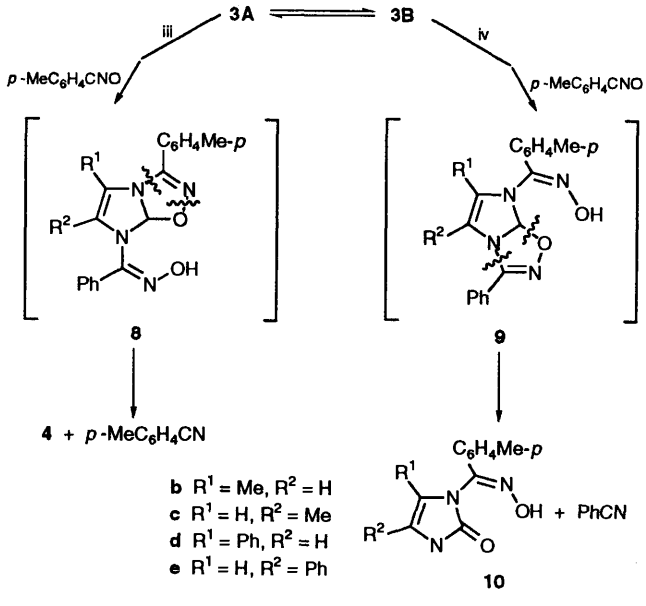
Scheme 2

The existence in solution of the two tautomers **3A** and **3B**, though not observed directly, was supported by trapping experiments.

One of these involved treating compound **3a** with *p*-toluonitrile oxide (TNO), either generated *in situ* from corresponding hydroxamoyl chloride and triethylamine or added after being prepared separately.[16] Instead of the product **4a** and *p*-toluonitrile alone being formed, which would have happened in the presence of only the open-form **3A**, benzonitrile was also obtained, with an inseparable 1:1 mixture of **4a** and its homologue **10a**.

This result can be explained (Scheme 3) if, under these conditions, we allow the existence of the above-mentioned equilibrium between the open-form **3Aa** and the closed-form **3Ba**. TNO reacts both with the open form, producing the intermediate **8**, and with the closed-form producing the intermediate **9**; the subsequent known cleavage of the oxadiazoline ring yields the products **4a** and *p*-toluonitrile, **10a** and benzonitrile, respectively.

Further confirmation of the presence in solution of both unsymmetrical tautomers **3A** and **3B** came from their reactions with TNO: components **3c** and **3e** provide (path iii) *p*-toluonitrile and the same imidazolones obtained by direct reaction of the BNO, *i.e.* **4c** and **4e**, respectively; **3b** and **3d** yield (path iv) benzonitrile and the homologues of the above-mentioned imidazolones **10b** and **10d** respectively (Table 1). For compounds **3c** and **3e**, where R^2 = Me or Ph, cycloaddition of TNO to imidazole C=N bond of open-form **3A** occurs, resulting in the non-isolated intermediate **8**, then products and toluonitrile. For isomers **3b** and **3d**, with R^2 = H, cycloaddition of TNO to the imidazole C=N bond of the open-form **3A** cannot occur, therefore it is form **3B** that reacts, and the TNO combines with the NH group to form the intermediate **9** which then gives the products **10** and benzonitrile. This is consistent with the above results as well as those of Caramella *et al.*[15]



Scheme 3

The structure of the compounds **10** were assigned on the basis of the analytical and spectroscopic data (Experimental Section).

An X-ray crystallographic analysis was carried out to confirm the structure of **4a·10a**. Tables of final fractional atomic coordinates, the full list of bond lengths and angles, and the list of thermal parameters have been deposited with the

Cambridge Crystallographic Data Centre.* Fig. 1 shows the molecular conformation for compounds **4a** and **10a**, both present in the crystal, and explains the numbering scheme; Fig. 2 shows the molecular packing of molecules in the unit cell with hydrogen bonds represented by a dotted line. The benzoyloxime group is linked to N(1) of the imidazole ring with the C(11)–N(1) bond distance of 1.429(3) Å. Steric requirements lead the oxime group to make a dihedral angle of 48.9° with respect to the heterocyclic ring, as shown by the torsion angles C(8)–N(1)–C(11)–N(3) 49.8(5)°. The imidazole ring and the carbonyl oxygen atom lie in the same plane [C(10)–O(1) 1.243(3) Å]. The deviations of each atom in the ring from the mean plane are very small, thus indicating some delocalization over this system. All the C–N and the N–N bond distances in the heterocyclic rings are intermediate between the expected single and double-bond lengths. The sum of the valence angles around N(1) are 359.3°, indicating no significant pyramidalization of these atoms. These results suggest that the imidazole rings have aromaticity and the hybridisation of exocyclic nitrogen atom is of the sp^2 type. However, steric requirements prevent the delocalization over benzoyl oxime moiety. C(11)–N(3) Bond distances are 1.275(7) Å, while N(3)–O(2) are 1.390(6) Å. These values are in the range 1.22 to 1.33 Å for the C–N and 1.357 to 1.439 Å for the N–O bonds[17] and are similar to those found in two reported *N*-benzoyl-1,2,4-triazole oximes.[18] The oxime configuration is *Z*. The aromatic ring (with normal geometry 1.385 Å and 120° for the average bond length and average internal angle respectively linked to C(11) at 1.468(3) Å makes an angle of 35.8(4)° with respect to the oxime fragment [as can be seen from C(6)–C(5)–C(11)–N(3) torsion angle]. The C(2)–C(1) single bond is of standard length [1.524(7) Å] while the C(1)–C(2)–C(7) and C(1)–C(2)–C(3) bond angles are significantly different [114.0(5)° and 126.8(5)° respectively]. Such a difference arises from the alternance in the crystal growth by two different molecules **4a** and **10a**. The molecular packing is essentially due to van der Waals interactions as well as to intermolecular hydrogen bonds, which connect two molecules in a dimeric arrangement through an inversion centre and two others for each, to form a three-dimensional network. The O···O and N···O distances are: N(2)···O(1) 2.72(2) Å O(1)···O(2) 2.96Å and O(W)···O(1)^{i} [(i) $1/2 + x$, $1/2 - y$, $1/2 - z$] 2.73(2) Å.

Another important aspect of this reaction between the *N*-unsubstituted imidazoles **1** and nitrile oxides concerns the formation of 1,4,2,5-dioxadiazine **2**. This unusual dimer of nitrile oxide was always isolated in our reaction and its presence suggests that the reaction proceeds through a zwitterionic intermediate, a finding perfectly consistent with the recent reports on other heteroaromatic bases and nitrile oxide in apolar solvent.[13b]

It is, therefore, probable that the initial course of the reaction involves the formation of the zwitterion **11**, which, under our conditions, can lead either to the dimerisation of BNO to dioxadiazine **2** or to the open-form **3A** product of nuecleophilic addition or to the electrocyclic closure to **3B** (Scheme 4). The

* For full details of the deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1993, issue 1.

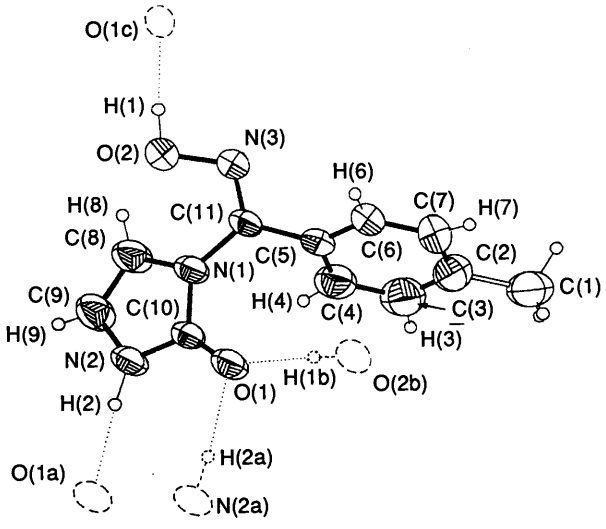
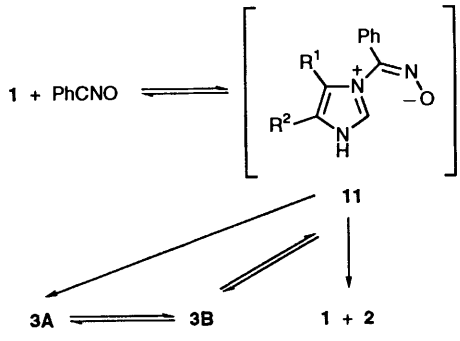


Fig. 1 Molecular conformation of compounds **4a** and **10a** within the **4a·10a** crystal



Scheme 4

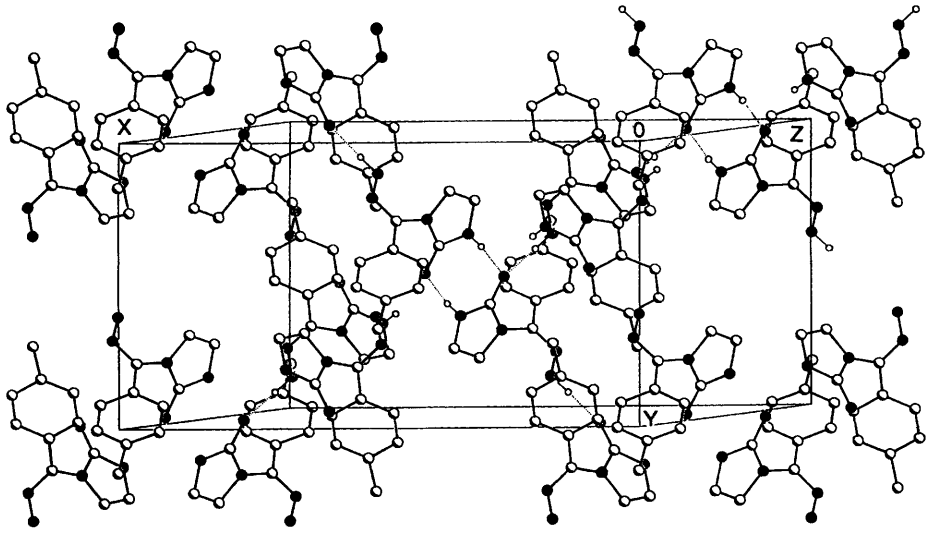


Fig. 2 Packing of molecules in the unit cell of crystal **4a·10a**

unusual dimerization of nitrile oxide to dioxadiazine is proof of the intermediacy of the zwitterion **11**, and indicates that the formation of the cycloadduct **3B** cannot be due to a concerted one-step, 1,3-cycloaddition. It must, therefore, proceed according to the proposed scheme and is linked to the equilibrium with tautomer **3A**, which, moreover, is the only form observed in the solid state.[9]

Experimental

M.p.s. were determined with a Reichert-Kofler hot-stage microscope and are uncorrected. Microanalyses were performed on a Carlo Erba EA 1102. IR spectra were recorded on a Perkin-Elmer 682 spectrometer ^{1}H and NMR spectra on a Hitachi-Perkin-Elmer R 24A (60 MHz) instrument using tetramethylsilane as internal reference and hexadeuteriodimethyl sulfoxide as solvent. *J* Values measured in Hz. Column chromatography was performed on Merck Kieselgel 70–270 mesh.

Reactions of the Imidazoles **1** *with Benzonitrile Oxide.*—Benzohydroximoyl chloride (20 mmol) in anhydrous benzene (80 cm^3) was added dropwise to a stirred solution of the imidazole **1** (10 mmol) and triethylamine (20 mmol) in boiling benzene (160 cm^3). After being heated under reflux for 2 h, the reaction mixture was cooled and the precipitate collected, washed with water (to remove the triethylammonium chloride) and crystallized from methanol–benzene to give the product **4**.

(Z)-3-*Benzoylimidazol*-2(3H)-*one oxime* **4a**. (4%), m.p. 219 °C (Found: C, 59.0; H, 4.4; N, 20.95. $C_{10}H_9N_3O_2$ requires C, 59.1; H, 4.46; N, 20.68%); ν_{max}(Nujol)/cm^{-1} 3450–3100 and 1675; δ_H 6.55 (2 H, s), 7.42 (5 H, s), 10.20 (1 H, s) and 11.75 (1 H, s).

(Z)-3-*Benzoyl*-4-*methylimidazol*-2(3H)-*one oxime* **4c**. (3%), m.p. 250 °C (Found: C, 60.55; H, 5.0; N, 19.5. $C_{11}H_{11}N_3O_2$ requires C, 60.82; H, 5.1; N, 19.35%); ν_{max}(Nujol)/cm^{-1} 3400–3100 and 1668; δ_H 1.79 (3 H, s), 6.33 (1 H, s), 7.45 (5 H, s), 9.93 (1 H, s) and 11.90 (1 H, s).

(Z)-3-*Benzoyl*-4-*phenylimidazol*-2(3H)-*one oxime* **4e**. (2%), m.p. 230 °C (Found: C, 68.6; H, 4.6; N, 15.2. $C_{16}H_{13}N_3O_2$ requires C, 68.80; H, 4.69; N, 15.05%); ν_{max}(Nujol)/cm^{-1} 3500–3100 and 1673; δ_H 7.00–7.92 (11 H, m), 10.90 (1 H, s) and 11.84 (1 H, s).

The benzene solution was evaporated under reduced pressure and the residue was chromatographed on silica gel. Elution with chloroform gave 1,4,2,5-dioxadiazine **2** (8–12%), 3,4-diphenylfuroxan (2–5%) and compound **3A** (68–75%).

1(Z)-1-*Benzoylimidazole oxime* **3a**. M.p. 194 °C (from acetone–light petroleum) (lit.,[5] 185 °C).

(Z)-1-*Benzoyl*-4-*Methylimidazole oxime* **3b**. M.p. 164 °C (Found: C, 65.5; H, 5.45; N, 21.0. $C_{11}H_{11}N_3O$ requires C, 65.67; H, 5.51; N, 20.88%); ν_{max}(KBr)/cm^{-1} 2800–2400, 1493, 1443, 1140, 1028 and 934; δ_H 2.15 (3 H, d, *J* 0.8), 6.98 (1 H, m, *J* 0.8 and 1.1), 7.40 (5 H, s), 7.78 (1 H, d, *J* 1.1) and 12.05 (1 H, s).

(Z)-1-*Benzoyl*-5-*methylimidazole oxime* **3c**. M.p. 205 °C (Found: C, 65.5; H, 5.4; N, 21.0. $C_{11}H_{11}N_3O$ requires C, 65.67; H, 5.51; N, 20.88%); ν_{max}(KBr)/cm^{-1} 2900–2200, 1491, 1443, 1105, 1028 and 935; δ_H 1.98 (3 H, d, *J* 0.8), 6.84 (1 N, m, *J* 0.8 and 1.0), 7.37 (5 H, s), 7.59 (1 H, d, *J* 1.0) and 12.30 (1 H, s).

(Z)-1-*Benzoyl*-4-*phenylimidazole oxime* **3d**. M.p. 195 °C (Found: C, 72.7; H, 4.9; N, 16.1. $C_{16}H_{13}N_3O$ requires C, 72.98; H, 4.98; N, 15.96%); ν_{max}(KBr)/cm^{-1} 2800–2200, 1496, 1442, 1108, 1028 and 931; δ_H 7.50–7.24 (11 H, m), 7.80 (1 H, s) and 12.18 (1 H, s).

(Z)-1-*Benzoyl*-5-*phenylimidazole oxime* **3e**. M.p. 205 °C (Found: C, 72.8; H, 4.9; N, 16.1. $C_{16}H_{13}N_3O$ requires C, 72.98; H, 4.98; N, 15.96%); ν_{max}(KBr)/cm^{-1} 2800–2300, 1494, 1444, 1160, 1068 and 978; δ_H 7.25 (1 H, d, *J* 1.1), 7.30–7.85 (10 H, m), 7.95 (1 H, d, *J* 1.1) and 12.15 (1 H, s).

Reaction of (Z)-1-*Benzoylimidazole Oximes* **3** *with Benzonitrile Oxide or with* p-*Toluonitrile Oxide.*—Triethylamine (20 mmol) in tetrahydrofuran (THF) (25 cm^3) was added to a stirred solution of the oxime **3** (10 mmol) and benzohydroximoyl chloride (20 mmol) or *p*-toluohydroximoyl chloride (20 mmol) in THF (100 cm^3). After the mixture had been heated under reflux for 2 h, the solid triethylammonium chloride was filtered off and washed with hot tetrahydrofuran. The combined filtrate and washings were evaporated under reduced pressure and the residue was chromatographed on silica gel. Elution with chloroform–ether (1:1) yielded, quantitatively, the products reported in Table 1.

(Z)-3-*Benzoylimidazol*-2-*one oxime*·(Z)-3-p-*toluoylimidazol*-2-*one oxime* **4a·10a**. This 1:1 adduct was isolated from **3a** with TNO, m.p. 207 °C; ν_{max}(Nujol)/cm^{-1} 3342, 3240–3120, 1687 and 1669; δ_H 2.31 (3 H, s), 6.45 (2 H, s), 6.55 (2 H, s), 7.42–7.20 (9 H, m), 10.18 (1 H, s), 10.20 (1 H, s), 11.64 (1 H, s) and 11.75 (1 H, s).

(Z)-4-*Methyl*-3-p-*toluoylimidazol*-2-*one oxime* **10b**. Isolated from **3b** with TNO, m.p. 210 °C (Found: C, 62.4; H, 5.6; N, 18.3. $C_{12}H_{13}N_3O_2$ requires C, 62.32; H, 5.67; N, 18.17%); ν_{max}(Nujol)/cm^{-1} 3240–3120 and 1676; δ_H 1.75 (3 H, s), 2.35 (3 H, s), 6.32 (1 H, s), 7.23–7.61 (4 H, m), 9.92 (1 H, s) and 11.85 (1 H, s).

(Z)-4-*Phenyl*-3-p-*toluoylimidazol*-2-*one oxime* **10d**. Isolated from **3d** with TNO, m.p. 218 °C (Found: C, 69.8; H, 5.2; N, 14.4. $C_{17}H_{15}N_3O_2$ requires C, 69.61; H, 5.15; N, 14.33%); ν_{max}(Nujol)/cm^{-1} 3240–3120 and 1683; δ_H 2.33 (3 H, s), 6.90–8.00 (10 H, m), 10.85 (1 H, s) and 11.70 (1 H, s).

Cleavage of Imidazol-2-one Oxime **4a**.—To a solution of **4a** (0.406 g, 2 mmol) in MeOH, (20 cm^3) 10% HCl (50 cm^3) was added. After the mixture had been heated under reflux for 3 h, the methanol was evaporated and the neutralized (5% $NaHCO_3$) aqueous phase was extracted with diethyl ether. The extract, after drying (Na_2SO_4) and evaporation of the solvent, afforded the 3-phenyl-1,2,4-oxadiazolin-5(4*H*)-one **5**, m.p. 204 °C (90%) (lit.,[11] 185 °C), identical with an authentic specimen.

Crystal Data for **4a·10a**.—$C_{10.5}H_{9.5}O_2N_3$, M = 474.64, monoclinic, $C2/c$, a = 19.760(3), b = 11.265(1), c = 12.200(2) Å, β = 127.53(2)°, V = 2153.6(4) Å^3, Z = 8, D_c = 1.29 g cm^{-3}, λ (Mo-Kα) = 0.71073 Å, μ = 0.87 cm^{-1}, F(000) = 876, T = 296 K, R = 0.048 for 1285 independent reflections.

Data collection and processing. Crystals suitable for X-ray analysis were obtained by recrystallization from methanol solution. A crystal of dimensions 0.18 × 0. 15 × 0.20 mm was used for intensity-data collection at 296 K with a Siemens R3/m four-circle diffractometer using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ and φ values of 25 strong reflections in the range $12 < 2\theta < 24°$. Crystal and electronic stability was confirmed by the constancy of three check reflections measured every 100 min of X-ray exposure. Of 1932 independent reflections measured by the $\omega/2\theta$ scan technique, in the range $3 < 2\theta < 46$ ($-23 < h < 18$, $0 < k < 13$, $0 < l < 14$), 1285 (R_{int} = 0.023) having net intensity $I < 3\sigma(I)$ were used in the solution and refinement of the Structure. Corrections for Lorentz and polarization effects were made, but not for absorption (μ = 0.87 cm^{-1}).

Structure determination. The structure was solved by direct methods with the MULTAN 80 system;[19] initially assuming molecule **4a** as the only one present in the asymmetric unit. The refinement of the coordinates for this molecule converged at R = 0.090. In the course of refinement, an additional peak of about 3 eÅ^{-3} was found at 1.50 from *C*2. This suggests that

compounds **4a** and **10a** are both 50% present in the cell. Refinement was anisotropically completed by full-matrix least-squares method assuming the residual peak as a methyl carbon atom of **10a**. After a few cycles, with an occupancy factor of 0.5 for *C*1, the refinement converged to the final value. Calculations were mainly carried out by the SHELX76[20] and PARST[21] systems of programs on the VAX-3400 computer at the 'Centro Interdipartimentale di Servizi per la Diffrattometria a Raggi-x dell'Università di Messina'. All the H atoms were found from the difference Fourier map and were refined, only the H atoms of the methyl group were added at calculated positions and included in the structure factor calculation with a common thermal parameter (U = 0.06 Å^2) and the appropriate occupancy factor. The final *R* values were $[\Sigma||F_o| - |F_o||]/\Sigma|F_o| = 0.048$ and $R_w[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.057$. The weighting scheme used in the last refinement cycle was $w = 1.000/[\sigma^2(F_o) + 0.001581\ F_o^2]$, G.O.F. = 1.557. Final difference map peaks were in the range 0.21, −0.24 eÅ^{-3}; max $\Delta/\sigma = 0.10$. Scattering factors for the non-hydrogen atoms were taken from ref. 22 and for H atoms from ref. 23.

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