Synthesis of Imidazole Derivatives Using 2-Unsubstituted 1*H*-Imidazole 3-Oxides

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The reaction of 1,4,5-trisubstituted 1*H*-imidazole 3-oxides **1** with Ac_2O in CH_2Cl_2 at 0–5° leads to the corresponding 1,3-dihydro-2*H*-imidazol-2-ones **4** in good yields. In refluxing Ac_2O, the *N*-oxides **1** are transformed to *N*-acetylated 1,3-dihydro-2*H*-imidazol-2-ones **5**. The proposed mechanisms for these reactions are analogous to those for *N*-oxides of 6-membered heterocycles (*Scheme 2*). A smooth synthesis of 1*H*-imidazole-2-carbonitriles **2** starting with **1** is achieved by treatment with trimethylsilanecarbonitrile (Me_3SiCN) in CH_2Cl_2 at 0–5° (*Scheme 3*).

Introduction. – The relevance of imidazole chemistry is clearly shown by the presence of this heterocycle in biologically important systems and by numerous applications of imidazole derivatives in pharmaceutical and agricultural chemistry [1][2]. For this reason, the elaboration of new syntheses of imidazole derivatives is of current interest. Among other important imidazole derivatives are 2*H*-imidazol-2-ones [3] and imidazole-2-carbonitriles ('2-cyanoimidazoles') [4][5]. Although it is well-known that heterocyclic *N*-oxides are versatile starting materials for the functionalization of the parent heterocycles [6][7], the application of imidazole *N*-oxides for this purpose is only rarely described.

In contrast to 6-membered N-heterocycles, the oxidation of imidazoles does not lead to the expected *N*-oxides (*cf.* [1b][8])[2]. Therefore, imidazole *N*-oxides are only available by cyclization of suitable open-chain precursors [2]. In a recent paper, we described the preparation of a series of 2-unsubstituted imidazole *N*-oxides by condensation of α-(hydroxyimino)ketones with methylidene alkylamines in EtOH solution [10]. A related procedure, which is based on the condensation of 1,4-diazabuta-1,3-dienes (1,2-diimines) or 2-iminopropanal dimethyl acetal with oximes in solution or under solvent-free conditions (SiO_2, alumina as solid support), was also reported [11].

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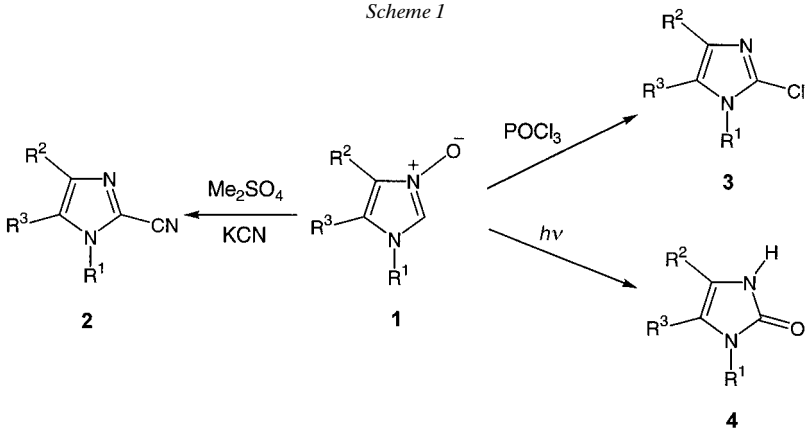
[2]) Attempted oxidations of 1-methyl-1*H*-benzimidazole derivatives with 3-chloroperbenzoic acid led to the formation of 2-[(3-chlorobenzoyl)oxy]-1*H*-benzimidazoles or 1,3-dihydro-2*H*-benzimidazol-2-ones in rather low yields [9].

Several years ago, *Ferguson* and *Schofield* described first synthetic applications of 2-unsubstituted imidazole *N*-oxides **1** for the functionalization of the ring system [12]. Treatment of **1** with Me_2SO_4 and KCN yielded 1*H*-imidazole-2-carbonitriles **2**, and the reaction with $POCl_3$ led to the chlorinated 1*H*-imidazoles **3** (*Scheme 1*). Deoxygenation of **1** was achieved either with PCl_3 [12] or with Zn/AcOH [13].

Scheme 1



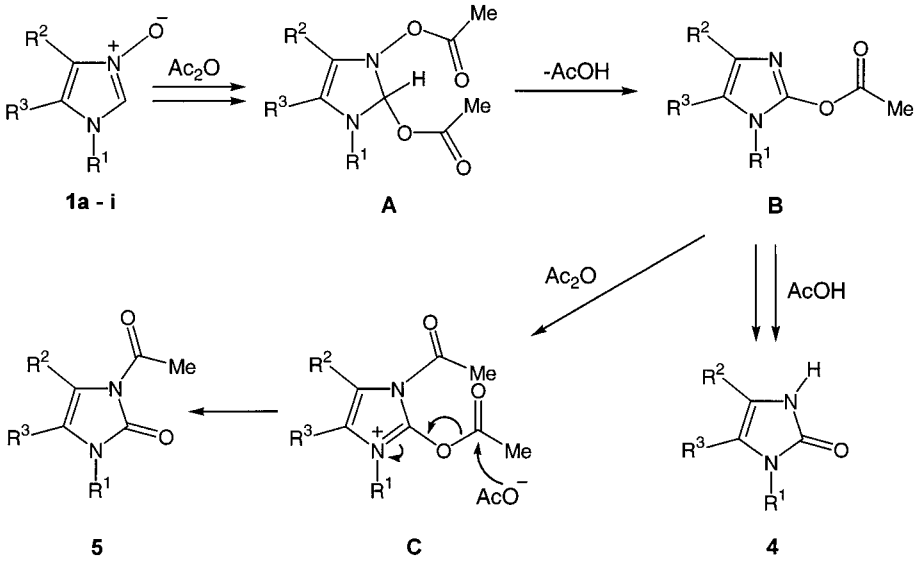
Another type of conversion of **1**, in which the O-atom remains in the molecule, is the photochemical isomerization to the corresponding 1,3-dihydro-2*H*-imidazol-2-one **4** [14][3]). On the other hand, matrix photolysis at 70 K of imidazole *N*-oxides of type **1** afforded products containing an N=C=O group, and this result is explained in terms of the formation of an oxaziridine intermediate and subsequent ring opening [16]. A further synthetic potential for compounds of type **1** is their reactivity as 1,3-dipoles. The first conversions of this type using phenyl isocyanate and dimethyl acetylenedicarboxylate as dipolarophiles were also described in [12]. Recently, we reported on reactions of **1** with thioketones, resulting in the formation of 1,3-dihydro-2*H*-imidazole-2-thiones [10]. The mechanism of this S-transfer reaction involved a [2 + 3] cycloaddition as the initial step.

In the present paper, we describe the thermal transformation of 1*H*-imidazole 3-oxides of type **1** into 1,3-dihydro-2*H*-imidazol-2-ones **4** and **5**, as well as a convenient route to 1*H*-imidazole-2-carbonitriles **2**. As already pointed out, both types of imidazole derivatives are of interest as building blocks in organic syntheses.

Results and Discussion. – The heating of solutions of 1*H*-imidazole 3-oxides **1a**–**h**, prepared according to [10], in Ac_2O for 10–60 min led to crystalline products **5a**–**h** in high yields (*Scheme 2*, *Table 1*). Their mass spectra and elemental analyses indicated that acetylated imidazolone derivatives were formed. Based on the IR and NMR data, an unambiguous differentiation between an *N*- and an *O*-acylated product was not possible. For example, the product **5a** of the reaction with 1,4,5-trimethyl-1*H*-imidazole 3-oxide (**1a**) showed 4*s* in the ^{13}C-NMR spectrum ($CDCl_3$) at 170.9, 152.6,

[3]) The photolysis of 2-phenyl-1*H*-imidazole 3-oxides led to ring opening and formation of *N*-benzoyl-1,4-diazabuta-1,3-dienes as the only product [15].

Scheme 2[a])



[a]) For R^1,R^2, and R^3, see *Table 1*.

Table 1. *1H-Imidazol-2(3H)-ones* **4** *and* **5** *Prepared by Treatment of* **1a**–**i** *with* Ac_2O

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**
R^1	Me	Et	$PhCH_2$	cHex	Me	cHex	$PhCH_2CH_2$	cHex	Me
R^2	Me	Me	Me	Me	Ph	Ph	Ph	Ph	Ph
R^3	Me	Me	Me	Me	Me	Ph	Ph	Me	Ph
4 (yield [%])[a])	–	–	**4c** (34)	–	**4e** (68)	**4f** (66)	**4g** (72)	**4h** (53)	**4i** (84)
5 (yield [%])[b])	**5a** (67)	**5b** (72)	**5c** (61)	**5d** (62)	**5e** (66)	**5f** (73)	**5g** (69)	**5h** (63)	–

[a]) Reaction of **1** in CH_2Cl_2 with Ac_2O at 0–5°. [b]) Reaction of **1** in refluxing Ac_2O.

117.8, and 113.3 ppm. The signal at 152.6 ppm could be attributed to C(2) of either a 1,3-dihydro-2*H*-imidazol-2-one or a 2-acetoxy-1*H*-imidazole. Moreover, the IR spectrum (KBr) showed only one strong absorption band at 1730 cm^{-1} accompanied by a rather weak one at 1690 cm^{-1}. Therefore, an X-ray crystal-structure determination of the product **5e** obtained from **1e** (*Scheme 2*, *Table 1*) was performed. The structure was established as 1-acetyl-1,3-dihydro-3,4-dimethyl-5-phenyl-2*H*-imidazol-2-one (**5e**, *Fig.*).

Comparison of the spectral data of **5e** with those of the other compounds **5** obtained in an analogous manner led us to the conclusion that *N*-acetylated derivatives were obtained in all cases. There are only a few compounds of this type reported so far. All of them were obtained by acylation of the corresponding 1,3-dihydro-2*H*-imidazol-2-ones [3][18]. In comparison with our reaction conditions, longer reaction times were required to complete the reactions in both protocols[4]). A comparable transformation

[4]) The structure of 1-acetyl-3-cyclohexyl-1,3-dihydro-5-methyl-4-phenyl-2*H*-imidazol-2-one prepared by *DeKimpe et al.* was also established by X-ray crystallography [3].

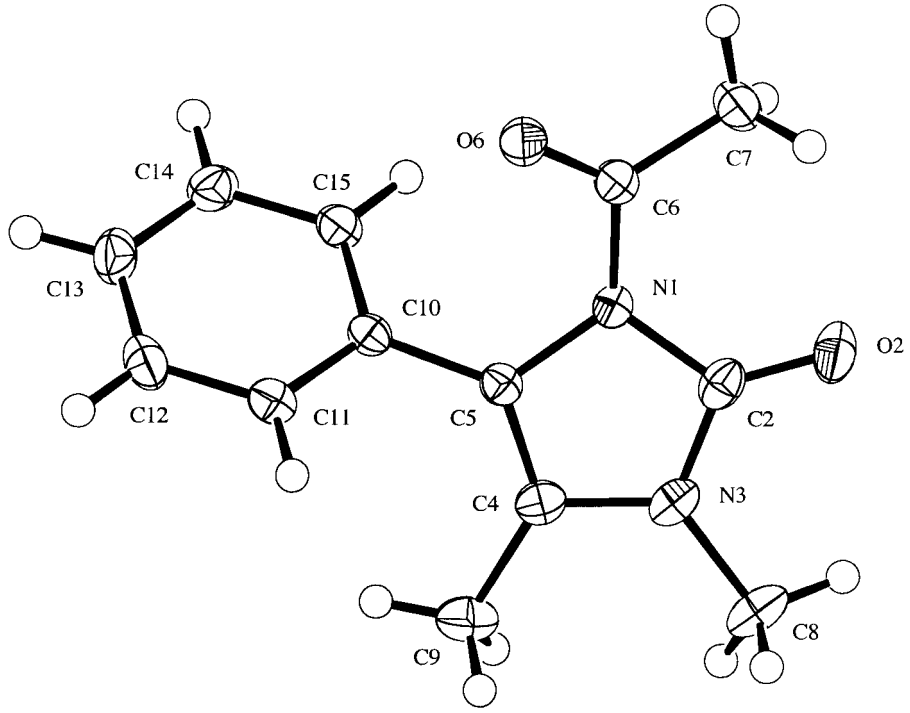


Figure. *ORTEP Plot* [17] *of the molecular structure of* **5e** (arbitrary numbering of the atoms; 50% probability ellipsoids)

has been reported by *Takahashi* and *Kano*: the reaction of 1-methyl-1*H*-benzimidazole 3-oxide in Ac_2O afforded 1-acetyl-1,3-dihydro-3-methyl-2*H*-benzimidazol-2-one [19].

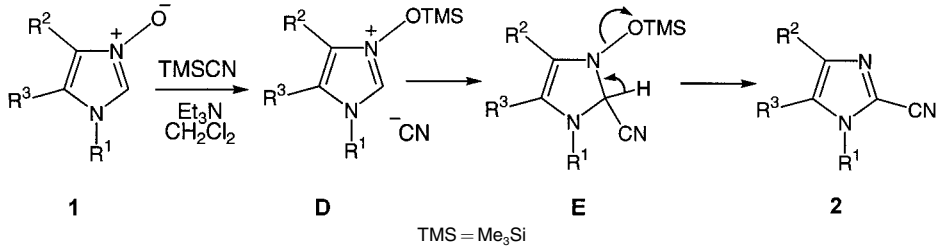
In contrast, the treatment of **1c**,**e**–**i** in diluted CH_2Cl_2 solution with a slight excess of Ac_2O, while keeping the temperature at 0–5°, led to 1,3-dihydro-2*H*-imidazol-2-ones **4c**,**e**–**i** as the only products (*Scheme 2*, *Table 1*).

In analogy to the mechanistic interpretation of the reaction of pyridine 1-oxide with Ac_2O leading to 2-acetoxypyridine [20], we propose the formation of intermediate **A** as the initial step followed by elimination of AcOH to give 2-acetoxy-1*H*-imidazole **B** (*Scheme 2*). In refluxing Ac_2O, a second acetylation to yield imidazolium species **C** is conceivable; deacetylation of the latter by cleavage of the AcO group leads to **5**. In dilute solution at room temperature, no *N*-acetylation takes place. The activation for the cleavage of the AcO group is achieved rather by protonation, and the deacetylation occurs again *via* nucleophilic attack of AcO^-. There are some formal similarities of these transformations with the *Polonovski* reaction [21], in which aliphatic *N*-oxides are treated with acid anhydrides to give an acid amide and an aldehyde *via* cleavage of one of the alkyl–N bonds. As in the case of **1**, the first step is the acylation of the *N*-oxide. Whereas in the *Polonovski* reaction an elimination of the carboxylic acid leads to an iminium ion, which subsequently adds a carboxylate ion, in the case of **1** an addition of the carboxylate ion to the primarily formed imidazolium salt leads to intermediate **A**, which, in turn, eliminates a carboxylic acid to give **B**.

In recent years, synthetic methods for the formation of C–C bonds by using silanes have been studied extensively [22]. Two frequently applied reagents are trimethyl(trifluoromethyl)silane (Me_3SiCF_3) [23] and trimethylsilanecarbonitrile (Me_3SiCN) [24]. In this paper, we report on the cyanation of imidazoles at C(2) starting with the corresponding 3-oxides **1**[5]). Fundamental work by *Vorbrüggen* on the cyanation of *N*-oxides of 6-membered heterocycles using Me_3SiCN opened new perspectives for the synthesis of cyano derivatives [28]. Using this method for the cyanation of 1-substituted 1*H*-imidazole 3-oxides led to mixtures of 2-, 4-, and 5-cyano-substituted imidazoles [29]. The ratio of the isomers depended on the solvent and the temperature of the reaction.

Following the methodology of cyanation of pyridine 1-oxides (*cf.* [28]), solutions of 1,4,5-trisubstituted 1*H*-imidazole 3-oxides **1** in dry CH_2Cl_2 in the presence of Et_3N and molecular sieves (4 Å)[6]) were treated with Me_3SiCN. The temperature of the mixture was kept at 0–5°, and the progress of the reaction was followed by TLC. After 1 h, the starting material had been consumed, in contrast to the procedure described in [29][7]). After chromatographic workup, imidazole-2-carbonitriles **2** were obtained in good yields (*Scheme 3*, *Table 2*). Careful drying of the substrate and the solvent, and addition of activated molecular sieves was essential to reach the reported yields of **2** and to limit the reaction time. For example, in the case of **1i**, which forms stable hydrates, the reaction carried out without activated molecular sieves led to a black mixture and tarry by-products, and the yield of **2i** dropped below 20%.

Scheme 3[a])



[a]) For R^1,R^2, and R^3, see *Table 2*.

The reaction mechanism for the formation of **2** is analogous to that proposed for the cyanation of azine *N*-oxides [28]: silylation of the *N*-oxide leads to the imidazolium ion **D**, which adds a CN^- ion to give **E** (*Scheme 3*). Smooth elimination of Me_3SiOH yields **2**.

5) Along with already cited methods for the cyanation of imidazole at C(2) [4][5][12], an electrophilic cyanation of lithiated 1-methyl-1*H*-imidazole with TsCN has been reported recently [25]. Nucleophilic substitution of 2,4-dibromo-1-methyl-5-nitro-1*H*-imidazole with NaCN gave the corresponding imidazolecarbonitrile [26]. Anodic cyanation of 1-methyl-1*H*-imidazoles yielded mixtures of 2-, 4-, and 5-cyano-substituted derivatives [27].

6) The molecular sieves were activated prior to their use by heating commercial 4-Å sieves with a gas flame for 15 min at 0.1 Torr.

7) Cyanation of 1-cyclohexyl-1*H*-imidazole 3-oxide was performed at 20, 40, and 60° with reaction times of 96, 24, and 17 h, respectively [29].

Table 2. *1*H-*Imidazole-2-carbonitriles* **2** *Prepared from* **1** *and* Me_3SiCN

	1a	**1c**	**1d**	**1f**	**1h**	**1j**
R^1	Me	$PhCH_2$	cHex	cHex	Me	$PhCH_2$
R^2	Me	Me	Me	Ph	Ph	Ph
R^3	Me	Me	Me	Ph	Ph	Ph
2 (yield [%])	**2a** (78)	**2c** (59)	**2d** (86)	**2f** (83)	**2h** (73)	**2j** (64)

In summary, smooth conversions of 2-unsubstituted 1*H*-imidazole 3-oxides **1** into 1,3-dihydro-2*H*-imidazol-2-ones **4**, 1-acetyl-1,3-dihydro-2*H*-imidazol-2-ones **5**, and 1*H*-imidazole-2-carbonitriles **2** were achieved. As the starting compounds **1** with various substituents are easily accessible, and as the procedures used led very efficiently to the products in high yields, the described methods are highly recommendable for the preparation of imidazole derivatives of type **2**, **4** and **5**.

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Experimental Part

1. *General*. M.p.: *Melt-Temp-II* apparatus (*Aldrich*); in capillary; uncorrected. IR Spectra: *Specord-75* IR spectrometer; in KBr; cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Varian-Gemini-200* or *Varian-VX-200* spectrometers; $CDCl_3$ solns.; chemical shifts δ in ppm rel. to $SiMe_4$ (= 0 ppm). MS: *VG-7070* or *Finnigan-MAT-90* instruments; EI at 70 eV; CI with NH_3; *m*/*z* (rel. %). Elemental analyses were performed in the *Galbraith Laboratory* (Knoxville, Tennessee) and microanalytical laboratory of the University of Zürich.

2. *Starting Materials.* Syntheses and properties of 1*H*-imidazole 3-oxides **1a**–**g** were described in [10]. *1-Cyclohexyl-5-methyl-4-phenyl-1*H-*imidazole 3-Oxide* (**1h**) was prepared according to [10] from 3-(hydroxyimino)-3-phenylpropan-2-one [30] and 1,3,5-tri(cyclohexyl)hexahydro-1,3,5-triazine [31]. Colorless crystals. M.p. 197–199° (Et_2O/CH_2Cl_2). IR (KBr): 3090*s*, 2950v*s*, 2880*s*, 1620*m*, 1450*s*, 1420*s*, 1340v*s* (br.), 1315*s*, 1230v*s*, 1200*s*, 1025*m*, 890*m*, 790*s*, 760*s*, 710*s*, 700v*s*. ^1H-NMR: 7.92 (*s*, CH); 7.65–7.35 (*m*, 5 arom. H); 3.90–3.85 (*m*, 1 H, cHex); 2.35–1.20 (*m*, 10 H, cHex). ^{13}C-NMR: 129.8, 127.4, 121.5 (3*s*, 1 arom. C, C(4), C(5)); 128.4, 128.2, 122.5 (3*d*, 5 arom. C); 55.6 (*d*, CH); 33.8, 25.5, 24.9 (3*t*, 5 CH_2). EI-MS: 256 (31, $M^{+\cdot}$), 240 (59), 174 (51), 157 (100), 130 (26), 104 (29), 89 (20), 77 (22). Anal. calc. for $C_{16}H_{20}N_2O$ (256.35): C 74.97, H 7.86, N 10.93; found: C 74.73, H 7.92, N 10.84.

Trimethylsilanecarbonitrile (Me_3SiCN) was a commercial reagent (*Aldrich*) distilled prior to use and stored in the refrigerator.

3. *Isomerization of 1*H-*Imidazole 3-Oxides* **1** *to 1,3-Dihydro-2*H-*imidazol-2-ones* **4**: *General Procedure.* To a stirred soln. of 1*H*-imidazole 3-oxide **1** (1 mmol) in abs. CH_2Cl_2 (1 ml) in a H_2O/ice cooling bath, a soln. of freshly distilled Ac_2O (0.5 ml (5.3 mmol)) in 1.5 ml of CH_2Cl_2 was added portionwise within *ca.* 10 min. The clear soln. was stirred until **1** was completely consumed (TLC monitoring; for reaction times, see data below). Then, the mixture was diluted with MeOH (2 ml) and stirring continued for another 5 min. The solvents were evaporated, and the solid residue was triturated with 80% EtOH (*ca.* 5 ml) and filtered under vacuum. Anal. pure products were obtained by recrystallization from an appropriate solvent.

*1-Benzyl-1,3-dihydro-4,5-dimethyl-2*H-*imidazol-2-one* (**4c**): After 1.5 h, 68.8 mg (34%). Colorless crystals. M.p. 195–197° (EtOH) ([32]: 197–201°). IR: 3300–2800*s* (br., NH), 1680v*s* (br., C=O), 1460*m*, 1430*m*, 1410*s*, 1365*m*, 815*m* (br.), 730*s*. ^1H-NMR: 10.25 (br. *s*, NH); 7.10 (br. *s*, 5 arom. H); 4.70 (*s*, CH_2); 1.79, 1.42 (2*s*, 2 Me). ^{13}C-NMR: 155.3 (*s*, C=O); 138.4 (*s*, 1 arom. C); 129.2, 128.9, 127.5 (3*d*, 5 arom. C); 114.1, 113.0 (2*s*, C(4), C(5)); 44.3 (*t*, CH_2); 9.4, 8.5 (2*q*, 2 Me).

*1,3-Dihydro-1,5-dimethyl-4-phenyl-2*H-*imidazol-2-one* (**4e**): After 15 min, 128.0 mg (68%). Colorless crystals. M.p. 246–251° (dec.) (EtOH) ([33]: 251–252°). IR: 3200–2800*s* (br., NH), 1680v*s* (br., C=O), 1600*m*, 1505*m*, 1465*m*, 1440*m*, 1400*m*, 1395*m*, 990*m*, 845*m* (br.), 760*m*, 740*s*. ^1H-NMR: 9.80 (br. *s*, NH); 7.40–7.20 (*m*, 5 arom. H); 3.21 (*s*, MeN); 2.21 (*s*, Me). ^{13}C-NMR: 154.5 (*s*, C=O); 130.9 (*s*, 1 arom. C); 129.2, 127.0, 126.5 (3*d*, 5 arom. C); 117.7, 116.4 (2*s*, C(4), C(5)); 27.2 (*q*, MeN); 9.8 (*q*, Me).

*1-Cyclohexyl-1,3-dihydro-4,5-diphenyl-2*H-*imidazol-2-one* (**4f**): After 15 min, 210.2 mg (66%). Colorless crystals. M.p. 286–290° (EtOH) ([34]: 297–298°). IR: 3200–2800v*s* (br., NH), 1685v*s* (br., C=O), 1600*m*, 1510*m*, 1450*m* (br.), 1375*s*, 840*m*, 765*m*, 760*m*, 755*m*, 695*s*. ^{1}H-NMR: 10.50 (br. *s*, NH); 7.50–7.20 (*m*, 5 arom. H); 7.10 (br. *s*, 5 arom. H); 3.60–3.40 (*m*, 1 H, cHex); 2.55–1.00 (*m*, 10 H, cHex). ^{13}C-NMR: 154.5 (*s*, C=O); 130.9, 130.3 (2*s*, 2 arom. C); 131.8, 129.5, 129.3, 128.8, 126.8, 125.8 (6*d*, 10 arom. C); 121.6, 118.6 (2*s*, C(4), C(5)); 54.6 (*d*, CH); 30.5, 26.2, 25.0 (3*t*, 5 CH_2).

*1,3-Dihydro-4,5-diphenyl-1-(2-phenylethyl)-2*H-*imidazol-2-one* (**4g**): After 25 min, 245.1 mg (72%). Colorless crystals. M.p. 244–247° ([13]: 236–238°). IR: 3300–2800*s* (br., NH), 1690v*s* (br., C=O), 1500*s*, 1450*s*, 1400*s*, 1360*s*, 1125*m*, 1030*m*, 960*m*, 760*s*, 700*s*. ^{1}H-NMR: 10.50 (br. *s*, NH); 7.40–6.80 (*m*, 15 arom. H); 3.78, 2.81 (2*t*, $J = 6.7$, 2 CH_2). ^{13}C-NMR: 154.4 (*s*, C=O); 138.9, 130.3, 127.0 (3*s*, 3 arom. C); 131.4, 129.4, 129.2, 128.8, 126.7, 125.9 (6*d*, 15 arom. C); 122.3, 118.9 (2*s*, C(4), C(5)); 43.0, 35.6 (2*t*, 2 CH_2).

*1-Cyclohexyl-1,3-dihydro-5-methyl-4-phenyl-2*H-*imidazol-2-one* (**4h**): After 15 min, 135.0 mg (53%). Colorless crystals. M.p. 244–246° (dec.) (hexane/CH_2Cl_2). IR: 3200–2750*s* (br., NH), 1680v*s* (C=O), 1500*w*, 1395*m*, 1370*m*, 1295*w*, 1265*w*, 1140*w*, 1000*w*, 890*w*, 835*m*, 800*m*, 770*m*, 750*s*, 695*s*. ^{1}H-NMR: 10.40 (br. *s*, NH); 7.45–7.20 (*m*, 5 arom. H); 3.80–3.60 (*m*, 1 H, cHex); 2.25 (*s*, Me); 2.15–1.10 (*m*, 10 H, cHex). ^{13}C-NMR: 153.4 (*s*, C=O); 129.7 (*s*, 1 arom. C); 127.5, 125.4, 125.3 (3*d*, 5 arom. C); 116.9, 114.5 (2*s*, C(4), C(5)); 52.5 (*d*, CH); 29.5, 25.0, 24.0 (3*d*, 5 CH_2); 9.2 (*q*, Me). EI-MS: 256 (23, $M^{+\cdot}$), 175 (12), 174 (100), 173 (15), 105 (15), 104 (18), 103 (11), 77 (18). Anal. calc. for $C_{16}H_{20}N_2O$ (256.35): C 74.97, H 7.86, N 10.93; found: C 74.54, H 7.90, N 10.82.

*1,3-Dihydro-1-methyl-4,5-diphenyl-2*H-*imidazol-2-one* (**4i**): After 15 min, 210.5 mg (84%). Colorless crystals. M.p. 286–290° (dec.) (EtOH) ([35]: 285–287°). IR: 3200–2600*s* (br., NH), 1680v*s* (br., C=O), 1600*m*, 1505*m*, 1460*s*, 1440*m*, 1395*s*, 1020*m*, 955*m*, 865*m*, 830*m*, 770*s*, 740*m*, 715*m*, 700*s*. ^{1}H-NMR: 9.90 (br. *s*, NH); 7.50–7.20 (*m*, 5 arom. H); 7.10 (br. *s*, 5 arom. H); 3.10 (*s*, MeN). ^{13}C-NMR: 154.7 (*s*, C=O); 130.2, 129.2 (2*s*, 2 arom. C); 131.1, 129.4, 129.0, 127.2, 126.1 (5*d*, 10 arom. C); 121.8, 118.5 (2*s*, C(4), C(5)); 28.3 (*q*, MeN).

4. *1-Acetyl-1,3-dihydro-2*H-*imidazol-2-ones* **5** *from 1*H-*Imidazole 3-Oxides* **1**: *General Procedure.* A soln. of **1** (1 mmol) in freshly distilled Ac_2O (2 ml) was heated under reflux. After 2 h, the mixture was cooled to r.t., and excess Ac_2O was distilled off (bulb-to-bulb). After trituration with EtOH (5 ml), the colorless residue afforded a crystalline product which was purified by recrystallization.

*1-Acetyl-1,3-dihydro-3,4,5-trimethyl-2*H-*imidazol-2-one* (**5a**): 112.7 mg (67%). Colorless crystals. M.p. 61–63°. IR: 1730v*s* (br., C=O), 1690*m*, 1430*m*, 1400*m*, 1375*s*, 1320*s*. ^{1}H-NMR: 3.15 (*s*, MeN); 2.64 (*s*, MeCO); 2.25, 1.97 (2*s*, 2 Me). ^{13}C-NMR: 170.9 (*s*, Me*C*O); 152.6 (*s*, C=O); 117.8, 113.3 (2*s*, C(4), C(5)); 27.1, 26.0, 11.8, 8.1 (4*q*, 4 Me). EI-MS: 168 (24, $M^{+\cdot}$), 127 (11), 126 (100), 125 (79), 111 (38), 97 (10), 56 (28). Anal. calc. for $C_8H_{12}N_2O_2$ (168.19): C 57.13, H 7.19, N 16.65; found: C 57.01, H 7.00, N 16.52.

*1-Acetyl-3-ethyl-1,3-dihydro-4,5-dimethyl-2*H-*imidazol-2-one* (**5b**): 132.0 mg (72%). Colorless crystals. M.p. 79–81°. IR: 1720v*s* (br., C=O), 1680*m* (C=O), 1460*m*, 1395*s*, 1370v*s*, 1310v*s*, 1040*w*, 955*m*. ^{1}H-NMR: 3.13 (*q*, $J = 7.3$, CH_2); 2.65 (*s*, MeCO); 2.25, 1.99 (2*s*, 2 Me); 1.23 (*t*, $J = 7.3$, Me). ^{13}C-NMR: 171.0 (*s*, Me*C*O); 152.0 (*s*, C=O); 117.3, 113.5 (2*s*, C(4), C(5)); 35.7 (*t*, CH_2); 26.1 (*q*, *Me*C=O), 14.6 (*q*, *Me*CH_2); 11.7, 8.0 (2*q*, 2 Me). EI-MS: 182 (20, $M^{+\cdot}$), 140 (100), 125 (19), 112 (32), 111 (22). Anal. calc. for $C_9H_{14}N_2O_2$ (182.22): C 59.32, H 7.74, N 15.37; found: C 59.07, H 7.71, N 14.98.

*1-Acetyl-3-benzyl-1,3-dihydro-4,5-dimethyl-2*H-*imidazol-2-one* (**5c**): 149.0 mg (61%). Colorless crystals. M.p. 51–53° (hexane/CH_2Cl_2). IR: 1720v*s* (br., C=O), 1680*m* (C=O), 1400*s*, 1380*s*, 1310v*s*, 1190*w*, 1130*w*, 730*w*, 710*w*. ^{1}H-NMR: 7.35–7.20 (*m*, 5 arom. H); 4.80 (*s*, CH_2); 2.68 (*s*, MeCO); 2.24, 1.87 (2*s*, 2 Me). ^{13}C-NMR: 170.9 (*s*, Me*C*O); 152.7 (*s*, CO); 136.8 (*s*, 1 arom. C); 128.7, 127.5, 126.8 (3*d*, 5 arom. C); 118.0, 113.7 (2*s*, C(4), C(5)); 44.3 (*t*, CH_2); 26.0 (*q*, *Me*CO); 11.7, 8.3 (2*q*, 2 Me). EI-MS: 244 (6, $M^{+\cdot}$), 202 (62), 167 (16), 149 (13), 135 (30), 121 (15), 111 (36), 105 (8), 104 (22), 92 (18), 91 (100, $C_7H_7^+$), 65 (15). Anal. calc. for $C_{14}H_{16}N_2O_2$ (244.29): C 68.83, H 6.60, N 11.47; found: C 68.54, H 6.61, N 11.17.

*1-Acetyl-3-cyclohexyl-1,3-dihydro-4,5-dimethyl-2*H-*imidazol-2-one* (**5d**): 146.5 mg (62%). Colorless crystals. M.p. 184–185° (hexane/CH_2Cl_2). IR: 1715v*s* (C=O), 1680*s* (C=O), 1410*w*, 1395*s*, 1390*s*, 1340*s*, 1195*w*, 980*w*, 770*w*, 600*w*. ^{1}H-NMR: 3.75–3.65 (*m*, 1 H, cHex); 2.61 (*s*, MeCO); 2.21, 1.98 (2*s*, 2 Me); 2.13–1.21 (*m*, 10 H, cHex). ^{13}C-NMR: 171.1 (*s*, Me*C*O); 152.0 (*s*, C=O); 117.7, 113.6 (2*s*, C(4), C(5)); 54.0 (*d*, CH); 30.4, 26.2, 25.2 (3*t*, *q*, 5 CH_2, *Me*CO); 11.8, 9.0 (2*q*, 2 Me). CI-MS: 237 (100, $[M+1]^+$), 209 (20). Anal. calc. for $C_{13}H_{20}N_2O_2$ (236.31): C 66.07, H 8.53, N 11.85; found: C 66.11, H 8.48, N 11.70.

*1-Acetyl-1,3-dihydro-3,4-dimethyl-5-phenyl-2*H-*imidazol-2-one* (**5e**): 152.0 mg (66%). Colorless crystals. M.p. 141–143° (hexane/CH_2Cl_2). IR: 1720v*s* (br., C=O), 1430*w*, 1370*s*, 1310*m*, 1275*s*, 765*m*, 740*w*, 710*w*. ^{1}H-NMR: 7.45–7.00 (*m*, 5 arom. H); 3.20 (*s*, MeCO); 2.60, 1.93 (2*s*, 2 Me). ^{13}C-NMR: 169.5 (*s*, Me*C*O); 152.8 (*s*, C=O); 131.2 (*s*, 1 arom. C); 129.8, 128.1, 127.7 (3*d*, 5 arom. C); 121.6, 117.5 (2*s*, C(4), C(5)); 27.4 (*q*, *Me*CO);

25.8 (*q*, MeN); 8.9 (*q*, Me). EI-MS: 230 (100, $M^{+\cdot}$), 189 (11), 188 (100), 187 (20). Anal. calc. for $C_{13}H_{14}N_2O_2$ (230.27): C 67.81, H 6.13, N 12.17; found: C 67.61, H 6.15, N 12.15.

*1-Acetyl-3-cyclohexyl-1,3-dihydro-4,5-diphenyl-2*H-*imidazol-2-one* (**5f**): 263.1 mg (73%). Colorless crystals. M.p. 151–153° (MeOH). IR: 1720v*s* (br., C=O), 1455*w*, 1380*m*, 1320*m*, 1285*m*, 1180*w*, 660*w*, 620*w*, 605*w*. ^{1}H-NMR: 7.35–7.02 (*m*, 10 arom. H); 3.46 (*m*, 1 H, cHex); 2.69 (*s*, MeCO); 2.30–1.07 (*m*, 10 H, cHex). ^{13}C-NMR: 169.8 (*s*, Me*C*O); 151.6 (*s*, C=O); 130.4, 128.3 (2*s*, 2 arom. C); 130.9, 129.6, 128.9, 128.5, 127.4, 127.2 (6*d*, 10 arom. C); 126.1, 118.7 (2*s*, C(4), C(5)); 55.1 (*d*, CH); 29.7, 26.1 (2*t*, 4 CH_2); 25.9 (*q*, *Me*CO); 24.9 (*t*, 1 CH_2). EI-MS: 360 (11, $M^{+\cdot}$), 319 (17), 318 (73), 236 (100), 193 (6), 105 (12), 104 (22). Anal. calc. for $C_{23}H_{24}N_2O_2$ (360.46): C 76.64, H 6.71, N 7.77; found: C 76.86, H 6.68, N 7.80.

*1-Acetyl-1,3-dihydro-4,5-diphenyl-3-(2-phenylethyl)-2*H-*imidazol-2-one* (**5g**): 263.9 mg (69%). Colorless crystals. M.p. 124–126° (EtOH). IR: 1720v*s* (br., C=O), 1445*w*, 1360*m*, 1305*m*, 1205*w*, 1120*w*, 795*w*, 740*w*, 700*m*. ^{1}H-NMR: 7.33–6.80 (*m*, 15 arom. H); 3.80, 2.81 (2*t*, $J = 7.5$, 2 CH_2); 2.65 (*s*, MeCO). ^{13}C-NMR: 169.9 (*s*, Me*C*O); 152.6 (*s*, C=O); 138.2, 130.6, 128.1 (3*s*, 3 arom. C); 130.9, 130.1, 129.2, 129.1, 127.9, 127.7, 127.0 (7*d*, 15 arom. C); 126.0, 119.3 (2*s*, C(4), C(5)); 43.5, 35.0 (2*t*, 2 CH_2); 26.1 (*q*, *Me*CO). CI-MS: 384 (25), 383 (100, $[M+1]^+$), 340 (4). Anal. calc. for $C_{25}H_{22}N_2O_2$ (382.46): C 78.51, H 5.80, N 7.32; found: C 78.88, H 5.79, N 7.29.

*1-Acetyl-3-cyclohexyl-1,3-dihydro-4-methyl-5-phenyl-2*H-*imidazol-2-one* (**5h**): 188 mg (63%). Colorless crystals. M.p. 112–113° (hexane). IR: 1725v*s* (br., C=O), 1370*s*, 1300*s*, 1280*m*, 765*w*, 750*w*, 710*w*. ^{1}H-NMR: 7.40–7.15 (*m*, 5 arom. H); 3.85–3.70 (*m*, 1 H, cHex); 2.62 (*s*, MeCO); 2.25–1.20 (*m*, 10 H, cHex); 1.98 (*s*, Me). ^{13}C-NMR: 169.3 (*s*, Me*C*O); 152.1 (*s*, C=O); 130.9 (*s*, 1 arom. C); 129.4, 127.7, 127.3 (3*d*, 5 arom. C); 120.9, 117.4 (2*s*, C(4), C(5)); 54.3 (*d*, CH); 30.2, 26.1 (2*t*, 4 CH_2); 25.8 (*q*, *Me*CO); 25.1 (*t*, 1 CH_2). EI-MS: 298 (5, $M^{+\cdot}$), 257 (7), 256 (41), 175 (12), 174 (100), 173 (15), 130 (7), 104 (11), 103 (8), 77 (6). Anal. calc. for $C_{18}H_{22}N_2O_2$ (298.38): C 72.46, H 7.43, N 9.39; found: C 72.00, H 7.41, N 9.16.

5. *Cyanation of 1*H-*Imidazole 3-Oxides* **1**. *General Procedure.* To a soln. of **1** (5 mmol, referring to the anh. form of **1**) in dry CH_2Cl_2 (4 ml), *ca.* 500 mg of freshly activated molecular sieves were added[6]). The mixture was stirred in a septum-closed 25-ml flask at r.t. for 1 h and then placed in a water/ice cooling bath. Subsequently, a soln. of trimethylsilanecarbonitrile (992.0 mg, 1.3 ml, 10 mmol) and Et_3N (759.0 mg, 1.05 ml, 7.5 mmol) in CH_2Cl_2 (3 ml) was slowly added through the septum using a syringe. The magnetic stirring was continued for 1 h at 0–5°. Then the yellow mixture was diluted with CH_2Cl_2 (20 ml) and extracted with H_2O (4 × 40 ml), the org. layer dried ($MgSO_4$) and evaporated and the yellow residue purified by prep. TLC (CH_2Cl_2). The 1*H*-imidazole-2-carbonitriles **2** were isolated as a fraction with R_f *ca.* 0.4–0.5, and additional crystallization afforded anal. pure samples.

*1,4,5-Trimethyl-1*H-*imidazole-2-carbonitrile* (**2a**): 527 mg (78%). M.p. 100–101° (Et_2O). IR: 2870*s*, 2205*s* (C≡N), 1560v*s*, 1470v*s*, 1440v*s*, 1390*s*, 1300*m*, 1220*m*, 1000*w*, 830*m*, 735*s*, 695*m*. ^{1}H-NMR: 3.68 (*s*, MeN); 2.22, 2.18 (2*s*, 2 Me). ^{13}C-NMR: 137.1 (*s*, C(2)); 128.5, 119.0 (2*s*, C(4), C(5)); 111.8 (*s*, C≡N); 31.9 (*q*, MeN); 12.8, 8.9 (2*q*, 2 Me). EI-MS: 136 (20, $[M+1]^+$), 135 (100, $M^{+\cdot}$), 134 (95), 120 (67), 93 (19), 79 (11), 68 (14), 67 (20). Anal. calc. for $C_7H_9N_3$ (135.17): C 62.20, H 6.71, N 31.09; found: C 62.19, H 6.81, N 30.99.

*1-Benzyl-4,5-dimethyl-1*H-*imidazole-2-carbonitrile* (**2c**): 623 mg (59%). M.p. 125–126° (hexane/CH_2Cl_2). IR: 2210*m* (C≡N), 1570*s*, 1450v*s*, 1430v*s*, 1390*m*, 1360*m*, 1310*m*, 1220*m*, 1140*w*, 1045*m*, 850*w*, 765*s*, 730v*s*, 700*s*. ^{1}H-NMR: 7.32 (br. *s*, 3 arom. H); 7.09 (br. *s*, 2 arom. H); 5.21 (*s*, CH_2); 2.20, 2.10 (2*s*, 2 Me). ^{13}C-NMR: 137.8 (*s*, C(2)); 134.3 (*s*, 1 arom. C); 128.8, 128.0, 126.6 (3*d*, 5 arom. C); 128.3, 119.1 (2*s*, C(4), C(5)); 111.6 (*s*, C≡N); 48.7 (*t*, CH_2); 12.6, 8.9 (2*q*, 2 Me). EI-MS: 212 (10, $[M+1]^+$), 211 (46, $M^{+\cdot}$), 92 (29), 91 (100, $C_7H_7^+$), 65 (32). Anal. calc. for $C_{13}H_{13}N$ (211.27): C 73.91, H 6.20, N 19.89; found: C 73.74, H 6.27, N 19.88.

*1-Cyclohexyl-4,5-dimethyl-1*H-*imidazole-2-carbonitrile* (**2d**): 874 mg (86%). M.p. 102–103° (hexane/Et_2O). IR: 2880v*s*, 2810*s*, 2205*s* (C≡N), 1565*s*, 1455*s*, 1430v*s*, 1390*s*, 1370*s*, 1350*m*, 1290*w*, 1220*w*, 1140*w*, 1000*w*, 905*m*, 845*w*, 785*m*. ^{1}H-NMR: 4.15–4.10 (*m*, 1 H, cHex); 2.35–1.15 (*m*, 10 H, cHex); 2.24, 2.17 (2*s*, 2 Me). ^{13}C-NMR: 136.9 (*s*, C(2)); 127.3, 116.6 (2*s*, C(4), C(5)); 112.7 (*s*, C≡N); 57.2 (*d*, CH), 32.0, 25.6, 24.5 (3*t*, 5 CH_2); 12.5, 9.3 (2*q*, 2 Me). EI-MS: 204 (10, $[M+1]^+$), 203 (39, $M^{+\cdot}$), 122 (77), 121 (100), 120 (31), 106 (12), 83 (48, $C_6H_{11}^+$), 80 (11). Anal. calc. for $C_{12}H_{17}N_3$ (203.39): C 70.90, H 8.43, N 20.67; found: C 71.11, H 8.59, N 20.64.

*1-Cyclohexyl-4,5-diphenyl-1*H-*imidazole-2-carbonitrile* (**2f**): 1.36 g (83%). M.p. 159–160° (MeOH). IR: 2880v*s*, 2800*m*, 2210*m* (C≡N), 1600*m*, 1500*m*, 1450v*s*, 1430*s*, 1405*m*, 1370*s*, 1340*s*, 1285*w*, 1170*w*, 1085*w*, 980*m*, 900*w*, 800v*s*, 740*s*, 705v*s*. ^{1}H-NMR: 7.53–7.17 (*m*, 10 arom. H); 3.85 (*m*, 1 H, cHex); 2.24–1.21 (*m*, 10 H, cHex). ^{13}C-NMR: 140.2 (*s*, C(2)); 132.9 (*s*, 2 arom. C); 132.5, 118.8 (2*s*, C(4), C(5)); 130.7, 129.9, 129.5, 128.3, 127.5, 126.9 (6*d*, 10 arom. C); 112.8 (*s*, C≡N); 57.4 (*d*, CH); 32.6, 25.9, 24.6 (3*t*, 5 CH_2). EI-MS: 328 (13, $[M+1]^+$), 327 (45, $M^{+\cdot}$), 246 (20), 245 (100), 244 (31). Anal. calc. for $C_{22}H_{21}N_3$ (327.40): C 62.20, H 6.71, N 31.09; found: C 62.19, H 6.81, N 30.99.

Table 3. *Crystallographic Data of Compound* **5e**

Crystallized from	MeOH
Empirical formula	$C_{13}H_{14}N_2O_2$
Formula weight [g mol^{-1}]	230.26
Crystal color, habit	colorless, tablet
Crystal dimensions [mm]	$0.18 \times 0.28 \times 0.50$
Temperature [K]	173(1)
Crystal system	monoclinic
Space group	$P2_1/n$
Z	4
Reflections for cell determination	25
2θ Range for cell determination [°]	38 – 40
Unit-cell parameters a [Å]	10.5031(8)
b [Å]	7.209(2)
c [Å]	16.2383(8)
β [°]	103.481(5)
V [Å^3]	1195.6(3)
D_x [g cm^{-3}]	1.279
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.0877
$2\theta_{(\max)}$ [°]	60
Total reflections measured	3918
Symmetry-independent reflections	3476
Reflections used [$I > 2\sigma(I)$]	2571
Parameters refined	211
Final R	0.0456
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0409
Goodness of fit	1.774
Secondary extinction coefficient	$1.8(2) \cdot 10^{-6}$
Final $\Delta_{\max}/\sigma$	0.0002
$\Delta\rho$ (max; min) [e Å^{-3}]	0.27; −0.20

*1-Methyl-4,5-diphenyl-1*H-*imidazol-2-carbonitrile* (**2h**): 945 mg (73%). M.p. 142 – 143° (MeOH) ([36]: 144.5 – 147°). IR: 2990*w*, 2205*s* (C≡N), 1600*w*, 1470*s*, 1450v*s*, 1400*w*, 1310*w*, 1230*w*, 1140*w*, 1035*w*, 975*m*, 805*m*, 795*m*, 770*s*, 700v*s*. ^{1}H-NMR: 7.50 – 7.20 (*m*, 10 arom. H); 3.58 (*s*, MeN). ^{13}C-NMR: 140.3 (*s*, C(2)); 132.7, 130.1 (2*s*, 2 arom. C); 132.5, 121.3 (2*s*, C(4), C(5)); 129.5, 128.8, 128.1, 127.7, 126.6 (5*d*, 6 arom. C); 111.2 (*s*, C≡N); 32.4 (*q*, Me). EI-MS: 260 (21, $[M+1]^+$), 259 (100, $M^{+\bullet}$), 258 (61), 244 (11), 243 (31). Anal. calc. for $C_{17}H_{13}N_3$ (259.31): C 78.74, H 5.05, N 16.20; found: C 78.86, H 5.15, N 16.10.

*1-Benzyl-4,5-diphenyl-1*H-*imidazole-2-carbonitrile* (**2j**): 1.07 g (64%). M.p. 116 – 117° (EtOH). IR: 2210*m* (C≡N), 1600*m*, 1500*s*, 1450v*s*, 1425*s*, 1335*s*, 1090*m*, 1040*m*, 985*m*, 825*m*, 780v*s*, 710v*s* (br.). ^{1}H-NMR: 7.50 – 7.40 (*m*, 5 arom. H); 7.30 – 7.15 (*m*, 8 arom. H); 6.95 – 6.75 (*m*, 2 arom. H); 5.20 (*s*, CH_2). ^{13}C-NMR: 140.9 (*s*, C(2)); 134.7, 132.6, 128.6 (3*s*, 3 arom. C); 132.5, 121.4 (2*s*, C(4), C(5)); 130.5, 129.7, 129.2, 128.8, 128.5, 127.5, 126.9 (7*d*, 15 arom. C); 111.5 (*s*, C≡N); 49.8 (*t*, CH_2). EI-MS: 336 (11, $[M+1]^+$), 335 (41, $M^{+\bullet}$), 91 (100, $C_7H_7^+$). Anal. calc. for $C_{23}H_{17}N_3$ (335.41): C 82.36, H 5.11, N 12.53; found: C 82.40, H 5.19, N 12.45.

6. *Crystal-Structure Determination of* **5e**[8]). All measurements were made on a *Rigaku-AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a 12-kW rotating anode generator. The $\omega/2\theta$ scan mode was employed for data collection. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Data collection and refinement parameters are given in *Table 3*, a view of the molecule is shown in the *Figure*. The structure was solved by direct methods using SHELXS97 [37].

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[8]) Crystallographic data (excluding structure factors) for structure **5e** reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-136002. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

The non-H-atoms were refined anisotropically. All of the H-atoms were located in a difference electron-density map, and their positions were allowed to refine together with individual isotropic displacement parameters. Refinement of the structure was carried out on F using full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o|-|F_c|)^2$. A correction for secondary extinction was applied. Neutral-atom scattering factors for non-H-atoms were taken from [38a] and the scattering factors for H-atoms from [39]. Anomalous dispersion effects were included in F_c [40]; the values for f' and f'' were those of [38b], and the values of the mass-attenuation coefficients were those of [38c]. All calculations were performed using the 'teXsan' crystallographic software package [41].

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