rotary evaporator. The residue was recrystallized to give 180 mg (85%) of **13a** as colorless crystals, mp 99–101 °C (ethanol–hexane). IR (KBr, cm^{-1}): 1642 (C=O). ^1H NMR ($CDCl_3$, $MeSi_4$, δ): 7.4–7.9 (m, 10 H, Ar–H), 8.1–8.5 (m, 5 H, OH and Ar–H).

***3,4,5-Tribenzoylpyrazole* (*13b*).** To a stirred solution of 73 mg (0.5 mmol) of benzoyldiazomethane (**12b**) in 3 mL of CH_2Cl_2, 117 mg (0.5 mmol) of **1** in 3 mL of CH_2Cl_2 was added. The stirring was continued for 24 h until the TLC showed disappearance of the starting compounds. TLC revealed only one spot. The solvent was removed with a rotary evaporator at room temperature and the residue was recrystallized from benzene–hexane to give 152 mg (80%) of **13b** as colorless crystals, mp 158–159 °C. IR (KBr, cm^{-1}) 1640 (C=O). ^1H NMR (Me_2SO, $MeSi_4$, δ): 7.2–8.1 (m, 15 H, Ar–H), 8.35 (s, 1 H, OH).

Registry No. **2a**, 3376-24-7; **2b**, 3376-23-6; **4a**, 104948-28-9; **4b**, 104948-29-0; **5a**, 1122-96-9; **5b**, 694-59-7; **7a**, 104948-30-3; **7b**, 104948-31-4; **8**, 1613-37-2; **9**, 104948-32-5; **10**, 1532-72-5; **11**, 104948-33-6; **12a**, 4203-31-0; **12b**, 3282-32-4; **12c**, 104975-85-1; **13a**, 104948-34-7; **13b**, 104948-35-8; PhOCC≡CCOPh, 1087-09-8.

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Heterocycles from Nitrile Oxides. 3. 1,2,4-Oxadiazol-5(4*H*)-ones

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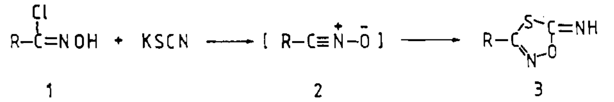
The reaction of nitrile oxides with potassium cyanate gives 3-aryl-1,2,4-oxadiazol-5(4*H*)-ones (5). These heterocycles are also obtained by cyclization of the corresponding *O*-carbethoxyamidoximes (7) with sodium ethoxide.

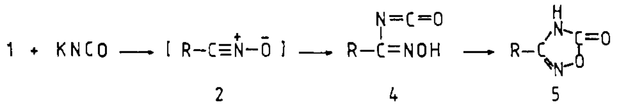
Introduction

In part 2 (*1*) of our research program, aiming at the synthesis of heterocycles from nitrile oxides, we described the synthesis of 1,2,4-oxadiazin-6-ones. As an extension of this program, we now report on the synthesis of 1,2,4-oxadiazol-5(4*H*)-ones from nitrile oxides. The reaction of nitrile oxides **2** with cyanate and thiocyanate anions has received only limited attention in the literature (*2*, *3*). Recently (*4*), we isolated stable 5-imino-Δ^2-1,4,2-oxathiazolines (**3**) from the reaction of potassium thiocyanate with nitrile oxides (Scheme I).

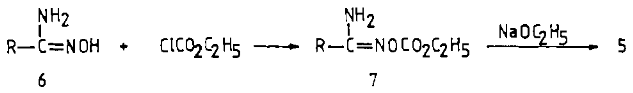
Scheme I



Scheme II



Scheme III



Results and Discussion

In the present study, the reaction of nitrile oxides with cyanate anion is investigated. It is found that potassium cyanate reacts readily with hydroxamoyl chlorides (**1**) (precursors of nitrile oxides) under mild conditions to give good yields of the corresponding 1,2,4-oxadiazol-5(4*H*)-ones (**5**) (Scheme II). These heterocycles are obtained as crystalline solids which are quite stable at room temperature.

Table I. Physical Data for Compounds 5

compd[a]	R	yield,[b] %	mp, °C	m/z(rel int) M$^{\bullet+}$	m/z(rel int) [RCNO]$^+$
5a	C_6H_5	65	198–200[c]	162 (84)	119 (100)
5b	o-$CH_3C_6H_4$	60	156–157	176 (96)	133 (10)
5c	p-BrC_6H_4	75	268–270	242/240 (100)	199/197 (80)
5d	p-$CH_3C_6H_4$	75	220–222[d]	176 (84)	133 (100)
5e	p-$NO_2C_6H_4$	70	308–310	207 (100)	164 (66)
5f	m-$NO_2C_6H_4$	70	140–141	207 (100)	164 (80)

[a] Elemental analyses (C, H, N) were submitted for review and agree well with the theoretical values. [b] Yields belong to method b in the Experimental Section. [c] Lit. (*5*) mp 203–205 °C. [d] Lit. (*6*) mp 221–222 °C.

The structure of compounds **5** is confirmed from spectral data and elemental analysis (Table I). Thus, the IR spectra of these compounds exhibit absorptions at about 1730–1760 cm^{-1} indicative of the C=O bond stretching. the N-H absorption of compounds **5b** and **5f** appear at 3260 and 3325 cm^{-1}, respectively, while compounds **5a,c,d,e** exhibit N-H absorption in the range 3120–3140 cm^{-1}. The mass spectra of compounds **5** are dominated by the correct molecular ion peaks together with fragment ions at M-43. The latter peak is assigned to the corresponding nitrile oxide ions, produced from the molecular ions by the expulsion of HNCO.

The 1,2,4-oxadiazol-5(4*H*)-ones (**5**) are also prepared by cyclization of the corresponding *O*-carbethoxyamidoximes (**7**) with sodium ethoxide (Scheme III). This lends further support

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Table II. Physical Data for Compounds 7

compd[a]	R	yield, %	mp, °C
7a	C_6H_5	80	110–111
7b	o-$CH_3C_6H_4$	70	67–68
7c	p-BrC_6H_4	85	129–131
7d	p-$CH_3C_6H_4$	90	120–121
7e	p-$NO_2C_6H_4$	85	128–130

[a] Elemental analyses (C, H, N) were submitted for review and agree well with the theoretical values.

to the proposed structure of compounds **5**. The amidoxime derivatives **7** are accessible by reacting the parent amidoximes **6** with ethyl chloroformate in the presence of triethylamine.

Compounds **7** show two N-H stretching bands at 3260–3495 cm^{-1}, in addition to a strong C=O stretching at 1745–1760 cm^{-1} (Table II). The ^1H NMR spectra of compounds **7** exhibit, besides the aromatic protons, a broad singlet at about δ 5 ppm (2 H), attributed to the NH_2 protons. The ethoxy hydrogens appear as a quartet centered at about δ 4.2–4.4 ppm (2 H) and a triplet at about 1.3–1.4 ppm (3 H).

Experimental Section

Melting points were determined on a Philip-Harris melting point apparatus and are uncorrected. The IR spectra (KBr) were measured on a Perkin Elmer 577 spectrophotometer. A Varian T-60A spectrometer was used to obtain the ^1H NMR spectra, with tetramethylsilane as the internal reference. The mass spectra were recorded on a Varian MAT 112 spectrometer using the direct inlet technique (EI, 70eV).

Hydroxamoyl chlorides were prepared by direct chlorination of aldoximes as described elsewhere (*4*). Amidoximes were synthesized from the corresponding nitriles and hydroxylamine hydrochloride following literature (*7–9*) procedures.

3-Aryl-1,2,4-oxadiazol-5(4H)-ones (5). (a) Potassium cyanate (15 mmol) and the particular hydroxamoyl chloride (10 mmol) were stirred in dry acetone (about 20 mL) overnight at room temperature. Water (50 mL) was then added and the precipitate was collected by filtration and crystallized from acetone–petroleum ether (bp 40–60 °C); yields were in the range of 50–65%.

(b) To a stirred solution of the *O*-carbethoxyamidoxime **7** (10 mmol) in absolute ethanol (20 mL), sodium (15 mmol) was added portionwise over a period of 10 min. The solvent was then removed in vacuo, and the residue acidified with 5% hydrochloric acid. The precipitate was filtered, air-dried, and crystallized.

O-Carbethoxyamidoximes (7). To a stirred solution of the amidoxime (20 mmol) in chloroform (40 mL) was added at room temperature a solution of ethyl chloroformate (22 mmol) in chloroform (10 mL). To this reaction mixture, triethylamine (30 mmol) was then added dropwise. The resulting mixture was finally stirred for 1 h at room temperature and then washed twice with water (2 × 50 mL). The organic layer was dried (anhydrous sodium sulfate) and the solvent evaporated. The solid residue was crystallized from chloroform–petroleum ether (bp 40–60 °C).

Registry No. **1a**, 698-16-8; **1b**, 74467-03-1; **1c**, 29203-58-5; **1d**, 36288-37-6; **1e**, 1011-84-3; **1f**, 33512-94-6; **5a**, 1456-22-0; **5b**, 26925-60-0; **5c**, 16672-19-8; **5d**, 31827-28-8; **5e**, 19932-97-9; **5f**, 24011-15-2; **6a**, 613-92-3; **6b**, 40312-14-9; **6c**, 19227-14-6; **6d**, 19227-13-5; **6e**, 1613-86-1; **7a**, 54752-10-2; **7b**, 104849-77-6; **7c**, 104849-78-7; **7d**, 31827-21-1; **7e**, 104849-79-8; potassium cyanate, 590-28-3; ethyl chloroformate, 541-41-3.

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A Convenient Synthesis of N,N′-Acylated Perimidones

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Several N-monoacylated and N,N′-diacylated perimidones were synthesized by quenching the intermediate resulting from the reaction between perimidone and *n*-butyllithium with the corresponding acylating reagent. The reactions were carried out under inert atmosphere in tetrahydrofuran at 0 °C. The prepared derivatives were identified on the bases of their NMR, IR, and elemental analysis data.

In the course of our study of the conformational analysis of 5- and 6-membered heterocyclic rings fused to benzene ring, we have reported the synthesis of several diacyl and diaroyl derivatives of benzimidazolone (*1*), benzimidazole (*2*), and tetrahydroquinoxaline (*3*). To extend the study, it was necessary to synthesize monoacylated and diacylated perimidone derivatives (II and III). No detectable yields were obtained with classical methods of acylation (*2*, *3*) except with the dibenzoyl derivative (*4*) (III; R = phenyl). However, good to excellent yields are obtained with the use of *n*-butyllithium. *n*-Butyllithium deprotonates the perimidone and renders the nitrogen atom more nucleophilic to react with the corresponding acid chloride or anhydride. The reaction pathway is shown in Scheme I. The structures and the physical properties of the

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