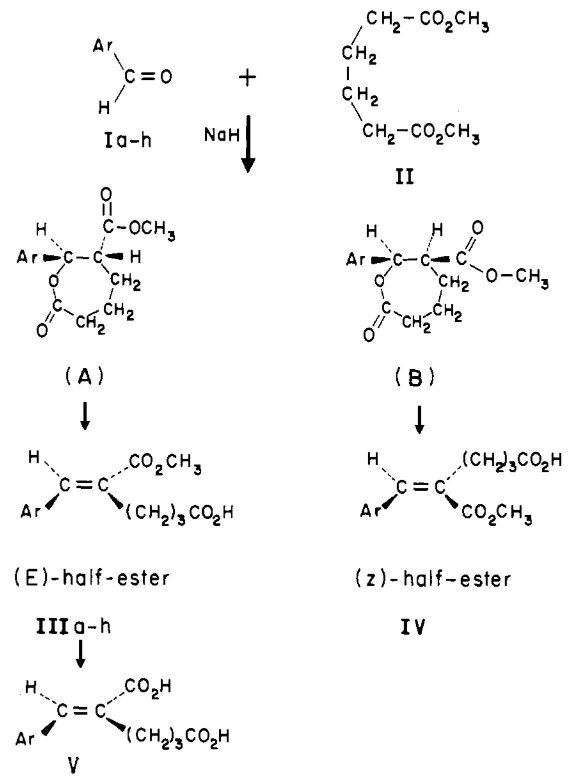
Scheme I



Compound	Ar	Compound	Ar	Compound	Ar
I,III,Va	C_6H_5	I,III,Vd	p-Br-C_6H_4	I,III,Vg	C_4H_3O
b	p-OCH_3-C_6H_4	e	O-Br-C_6H_4	h	$C_{10}H_7$
c	p-CH_3-C_6H_4	f	m-Cl-C_6H_4		

flame ionization detector was employed for purity analysis. The samples were treated with TMCS prior to GLC analysis.

Preparation of the Half-Esters IIIa-h. The dimethyl adipate (0.12 mol), aldehyde (0.1 mol), and sodium hydride (0.15 mol) are stirred in excess dry benzene with occasional cooling to prevent rise of temperature above 40 °C (few drops of methanol are added to initiate the reaction) the reaction mixture was left overnight by room temperature and then worked up as previously reported (*5*). The residue was crystallized from *n*-hexane or cyclohexane to produce 5-methoxycarbonyl-6-(aryl)-hex-5-enoic acids (IIIa-h).

Saponification of the Half-Esters IIIa-h. The half-ester (2 g) was refluxed with 15% aqueous alcoholic potassium hydroxide solution (15 g KOH, 50 mL H_2O, and 50 mL methanol) for 4 h. The alcohol was distilled off, and the cold alkaline solution was acidified with cold dilute HCl. The resulting dibasic acid was taken in ether, washed with cold distilled water, and dried (Na_2SO_4) and the ether was removed. Crystallization of the acids with *n*-hexane gave 5-carboxy-6-(aryl)-hex-5-enoic acids (Va-h).

Registry No. Ia, 100-52-7; Ib, 123-11-5; Ic, 104-87-0; Id, 1122-91-4; Ie, 6630-33-7; If, 587-04-2; Ig, 98-01-1; Ih, 66-77-3; IIIa, 105064-44-6; IIIb, 105064-45-7; IIIc, 105064-46-8; IIId, 105064-47-9; IIIe, 105064-48-0; IIIf, 105064-49-1; IIIg, 105064-50-4; IIIh, 105064-51-5; Va, 105064-52-6; Vb, 105064-53-7; Vc, 105064-54-8; Vd, 105064-55-9; Ve, 105064-56-0; Vf, 105064-57-1; Vg, 105064-58-2; Vh, 105064-59-3; dimethyl adipate, 627-93-0.

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Reactions of Dibenzoylacetylene with *N*-Alkylnitrones, Heteroaromatic *N*-Oxides, and Diazo and Azoxy Compounds

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Dibenzoylacetylene affords 4-oxazolines, enamines, and pyrazoles by reaction with *N*-alkylnitrones, heteroaromatic *N*-oxides, and aryl diazo compounds, respectively. However, azoxy compounds did not react with dibenzoylacetylene.

We have recently reported (*1*) that the reaction of dibenzoylacetylene (**1**) with *N*-arylnitrones follows a different path from those with other alkynes (*2*). 3-Anilino-1,4-diphenylbutane-1,2,4-trione and the corresponding aldehydes were obtained from the reaction of **1** with those *N*-arylnitrones (*1*). These results prompted us to extend this reaction to *N*-alkylnitrones **2a,b** and other 1,3-dipolar heteroaromatic *N*-oxides **5a,b**, **8**, and **10**, and diazo **12a-c** and azoxy **14a,b** compounds (see Experimental Section), to investigate the behavior of this alkyne **1** toward these 1,3-dipoles.

The reaction of *N*-alkylnitrones **2a,b** with the dipolarophile yielded the 4-oxazolines **4a,b** as sole products (Figure 1). The structure of 4-oxazoline was assigned to these products **4a,b** on the basis of their analytical and spectroscopic data (see Experimental Section). Observation of the methine proton signal

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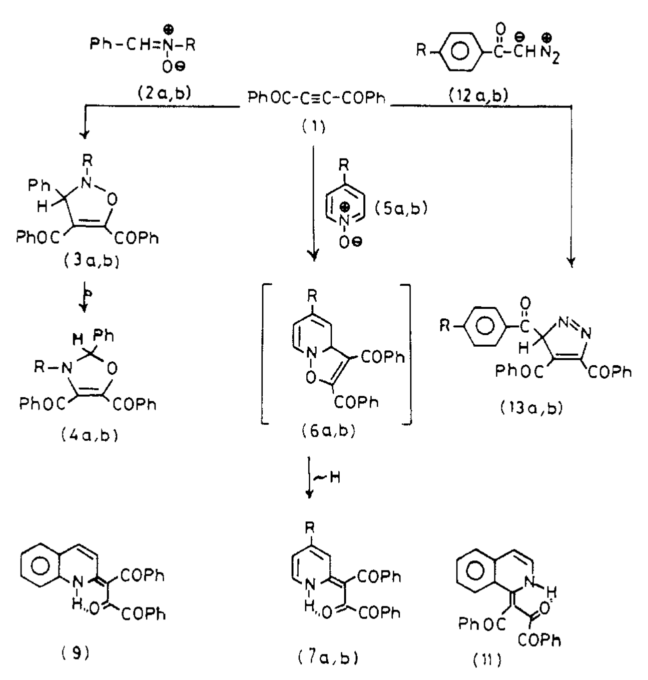

Figure 1.

at 5.90 and 6.10 ppm in their NMR spectra is indicative of the methine group being located between an oxygen and a nitrogen atom (*3-6*).

On the other hand, the addition of **1** to the heteroaromatic *N*-oxides **5a,b**, **8**, and **10** under the same conditions yielded solely the ring-opened enamines **7a,b**, **9**, and **11**, respectively (Figure 1). The infrared spectra of these enamines **7a,b**, **9**, and **11** showed absorption maxima in the amino group region 3350, 3400, 3450, and 3100 cm^{-1}, respectively. The observation of a doublet from doublet and a doublet in the NMR spectra of **7a** and **11** at relatively high magnetic field (6.7 and 7.05 ppm) give additional evidence for the olefinic structure of these enamines, as compared to the chemical shifts of the pyridine and isoquinoline protons 7.1-8.5 and 7.5-8.5 ppm, respectively (*7*). Moreover, the ^{13}C chemical shift values observed in the NMR spectra of **7a**, **9**, and **11** at 111.30-117.25 ppm for olefinic carbons, further support the structure suggested (Figure 1).

Neither the diazophosphonium salt **12c** nor the aryl azoxy compounds **14a,b** reacted with the dipolarophile **1**, even on prolonged heating.

Experimental Section

Melting points, uncorrected, were determined on a Gallenkamp device. Infrared spectra were recorded on a Shimadzu-408 spectrophotometer using KBr disk. ^1H and ^{13}C NMR spectra were obtained with Varian EM-360 (60 MHz) and Bruker WP 80 spectrometers. Mass spectra were determined on a MAT 311A spectrometer operating at (70 eV). Elemental analyses were performed by the microanalytical unit at Cairo University. All the reaction products gave satisfactory analytical data. The dibenzoylacetylene (**1**) (*10*), nitrones **2a,b** (*11*, *12*), and diazo compounds, 4-nitrobenzoyldiazomethane (**12a**), benzoyldiazomethane (**12b**), and (1-diazoxopropyl)triphenylphosphonium tetrafluoroborate (**12c**) (*8*) were prepared according to the literature. The heteroaromatic *N*-oxides, 4-methoxypyridine *N*-oxide (**5a**), pyridine *N*-oxide (**5b**), quinoline *N*-oxide (**8**), and isoquinoline *N*-oxide (**10**), and azoxy compounds, 4,4'-azoxyanisole (**14a**) and azoxybenzene (**14b**), were purchased from Aldrich and used without further purification. A 1-mm layer of silica gel Merck PF_{254} on plates 20 cm by 48 cm was employed for preparative thin-layer chromatography (TLC) and bands were detected by exposure to short-wavelength ultraviolet.

Reaction of Nitrone 2a and 1. A solution of 234.2 mg (1.0 mmol) of **1** in 3 mL of CH_2Cl_2 was added to a stirred solution of 177.2 mg (1.0 mmol) of **2a** in 3 mL of CH_2Cl_2. The stirring was continued 24 h until the TLC showed disappearance of the starting compounds. TLC revealed only one spot. The solution was concentrated with a rotary evaporator at room temperature. Upon addition of hexane and cooling colorless crystals 380 mg (92%) of 3-*tert*-butyl-4,5-dibenzoyl-2-phenyl-4-oxazoline (**4a**), mp 121 °C, were obtained. IR (KBr, cm^{-1}): 1668 (C=O); 1615 (C=C). ^1H NMR ($CDCl_3$, Me_4Si, δ): 1.25 (s, 9 H, $C(CH_3)_3$); 5.90 (s, 1 H, OCHN); 6.80-7.80 (m, 15 H, Ar-H).

Reaction of Nitrone 2b and 1. To a stirred solution of 135.2 mg (1.0 mmol) of **2b** in 3 mL of CH_2Cl_2, 234 mg (1.0 mmol) of **1** in 3 mL CH_2Cl_2 was added. The stirring was continued for 48 h and then the solution was concentrated with rotary evaporator at room temperature. The residue was then chromatographed on a TLC using a mixture of benzene-ethyl acetate (10:1) as eluent, to give one zone (R_f = 0.52). Extraction with acetone and crystallization afforded 278 mg (78%) 4,5-dibenzoyl-3-methyl-2-phenyl-4-oxazoline (**4b**) as colorless crystals, mp 102-104 °C (ethanol-hexane). IR (KBr, cm^{-1}): 1665 (CO). ^1H NMR ($CDCl_3$, $MeSi_4$, δ): 1.35 (s, 3 H, CH_3), 6.10 (s, 1 H, OCHN), 6.95-7.90 (m, 15 H, Ar-H).

Reaction of Heteroaromatic N-Oxides 5a,b, 8 as well as 10 with 1. General Procedure. To stirred solution of 1 mmol of heteroaromatic *N*-oxide in 5 mL of chloroform, 1 mmol of **1** in 2 mL of chloroform was added. The stirring was continued for 10-12 h at room temperature until the TLC showed the disappearance of the starting compounds. The solvent was then removed at room temperature with a rotary evaporator and the residue was crystallized from the proper solvent to give the products **7a,b**, **9**, and **11**.

1,4-Diphenyl-3-(4-methoxy-1,2-dihydro-2-pyridylidene)butane-1,2,4-trione (7a). Recrystallization from CH_2Cl_2-hexane gave pale yellow crystals 245 mg (68%) of **7a**, mp 253-254 °C. IR (KBr, cm^{-1}): 3350 (NH); 1680, 1630 (C=O). ^1H NMR (Me_2SO, $MeSi_4$, δ): 4.05 (s, 3 H, OCH_3), 6.70 (dd, 1 H, J = 3 Hz, J = 9 Hz, 5-H), 7.10-8.25 (m, 13 H, Ar-H and NH). ^{13}C NMR (Me_2SO, $MeSi_4$, δ): 112.25 and 114.50 (olefinic carbon). MS (70 eV, *m/e*, rel intensity): 359 (9, M^+), 328 (5), 254 (100), 226 (5).

1,4-Diphenyl-3-(1,2-dihydro-2-pyridylidene)butane-1,2,4-trione (7a). Recrystallization from ethanol afforded 190 mg (55%) as yellow crystals of **7b**, mp 137-139 °C. IR (KBr, cm^{-1}): 3400 (NH), 1658 (C=O).

1,4-Diphenyl-3-(1,2-dihydro-2-quinolylidene)butane-1,2,4-trione (9). Recrystallization from CH_2Cl_2-hexane gave 180 mg (69%) as yellow crystals of **9**, mp 250-251 °C (decomposes). IR (KBr, cm^{-1}): 3450 (NH), 1685 (C=O). ^1H NMR (Me_2SO, $MeSi_4$, δ): 7.20-8.10 (m, 15 H, NH and Ar-H), 8.45 (d, 2 H, J = 6 Hz, Ar-H). ^{13}C NMR (Me_2SO, $MeSi_4$, δ): 111.30, 114.49, and 117.25 (three olefinic carbon). MS (70 eV, *m/e*, rel intensity): 379 (9, M^+), 274 (100), 246 (7).

1,4-Diphenyl-3-(1,2-dihydro-1-isoquinolylidene)butane-1,2,4-trione (11). Recrystallization from $CHCl_3$-hexane gave 190 mg (73%) as yellow crystals of 11 mp 210-211 °C (decomposes). IR (KBr, cm^{-1}): 3100 (NH), 1645 (C=O). ^1H NMR ($CDCl_3$, $MeSi_4$, δ): 7.05 (d, 1 H, J = 7 Hz, C=CH), 7.20-7.95 (m, 15 H, NH and Ar-H), 8.80 (d, 1 H, J = 7 Hz, C=CH—N). ^{13}C NMR ($CDCl_3$, $MeSi_4$, δ): 112.65, 114.60, and 116.30 (three olefinic carbon). MS (70 eV, *m/e*, rel intensity): 379 (15, M^+), 274 (100), 246 (25).

3,4-Dibenzoyl-5-(4-nitrophenyl)pyrazole (13a). A 95.6-mg (0.5 mmol) sample of 4-nitrobenzoyldiazomethane (**12a**) in 3 mL of CH_2Cl_2 was added to a solution of 117 mg (0.5 mmol) of **1** in 3 mL of CH_2Cl_2. The mixture was stirred for 24 h until the TLC showed the disappearance of the starting compounds. The solvent was then removed at room temperature with a 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). ^{1}H 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$_2$Cl$_2$, 117 mg (0.5 mmol) of **1** in 3 mL of CH$_2$Cl$_2$ 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). ^{1}H NMR (Me$_2$SO, 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).

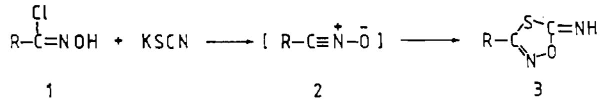
Results and Discussion

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.

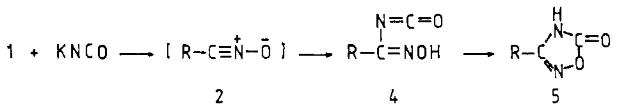
The structure of compounds **5** is confirmed from spectral data and elemental analysis (Table I). Thus, the IR spectra of these compounds exhibit absorptions at about 1730–1760 cm^{-1} indicative of the C=O bond stretching. the N-H absorption of compounds **5b** and **5f** appear at 3260 and 3325 cm^{-1}, 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

Scheme I



Scheme II



Scheme III

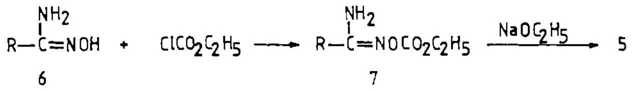


Table I. Physical Data for Compounds 5

				m/z(rel int)	
compd[a]	R	yield,[b] %	mp, °C	M$^{\bullet+}$	[RCNO]$^+$
5a	C$_6$H$_5$	65	198–200[c]	162 (84)	119 (100)
5b	*o*-CH$_3$C$_6$H$_4$	60	156–157	176 (96)	133 (10)
5c	*p*-BrC$_6$H$_4$	75	268–270	242/240 (100)	199/197 (80)
5d	*p*-CH$_3$C$_6$H$_4$	75	220–222[d]	176 (84)	133 (100)
5e	*p*-NO$_2$C$_6$H$_4$	70	308–310	207 (100)	164 (66)
5f	*m*-NO$_2$C$_6$H$_4$	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.

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