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One-pot three-component reaction of isocyanides, dialkyl acetylenedicarboxylates and phthalhydrazide: synthesis of highly functionalized 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones

Mohammad Bagher Teimouri*

Petrochemical Department, Iran Polymer and Petrochemical Institute, PO Box 14965-115, Tehran 1497713115, Iran

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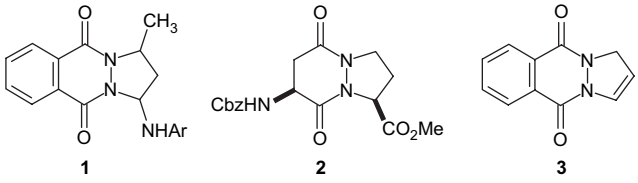
Abstract—Protonation of the highly reactive 1:1 intermediate produced in the reaction between alkyl isocyanides and electron-deficient acetylenic esters with phthalhydrazide, leads to a vinylisonitrilium cation, which undergoes an addition reaction with the conjugate base of the phthalhydrazide to produce dialkyl 3-(alkylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylates in fairly good yields at room temperature.

1. Introduction

Nitrogen-containing heterocyclic compounds are widespread in nature, and their applications to biologically active pharmaceuticals, agrochemicals, and functional materials are becoming more and more important.[1] The development of new efficient methods to synthesize *N*-heterocycles with structural diversity is one major interest of modern synthetic organic chemists.[2] Among a large variety of nitrogen-containing heterocyclic compounds, heterocycles containing bridgehead hydrazine have received considerable attention because of their pharmacological properties and clinical applications.[3] For example, 1-arylamino-2,3-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives **1** were reported to possess antiinflammatory, analgesic, antihypoxic, and antipyretic properties.[4] Furthermore, pyrazolidine compounds have been converted into azaproline amino acids, which have been studied upon incorporation into traditional peptides as well as small molecule peptidomimetics **2**.[5]

So far, only a few procedures have been described in the literature for the preparation of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione skeleton **3**. In 1937, Drew and Hatt reported the first synthesis of this triheterocyclic structure via the reaction between phthalhydrazide and cinnamaldehyde.[6] Recently, Sinkkonen and co-workers reexamined the cycloaddition reactions of cyclic hydrazides of dicarboxylic acids (such as maleic and phthalic acids) and α,β-unsaturated carbonyl compounds leading to the formation of 1-amino-2,3-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones. They also studied their structures by NMR and mass spectrometric methods and theoretical calculations.[7] Moreover, the oxidation of phthalhydrazide with lead tetraacetate in the presence of furfural derivatives in methylene chloride afforded 5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]-phthalazine-1-carboxylic acids in moderate yields (Scheme 1).[8]



1 **2** **3**

Scheme 1.

The nucleophilic addition of alkyl or aryl isocyanides to electron-deficient acetylenic esters such as dimethyl acetylenedicarboxylate (DMAD) is well documented.[9] It has been shown that alkyl or aryl isocyanides add to dialkyl acetylenedicarboxylates to generate zwitterionic species, which serve as intermediates in many different reactions.[10–13] Recently, these highly reactive zwitterionic intermediates have been captured by suitable CH–,[11] NH–,[12] and OH-acids[13] substrates such as (ethoxycarbonylmethyl)triphenylphosphonium bromide,[11j] 1,2-diacylhydrazines,[12f] and benzoic acids,[13d] which produced *N*-alkyl-2-triphenylphosphoranylidene glutarimides, 1*H*-pyrazoles and butenedioate derivatives, respectively.

Keywords: Dialkyl acetylenedicarboxylate; Isocyanide; Multicomponent reaction; Phthalhydrazide; 1*H*-Pyrazolo[1,2-*b*]phthalazine.
* Corresponding author. Tel.: +98 21 44580000; fax: +98 21 44580032; e-mail: m.teimouri@ippi.ac.ir

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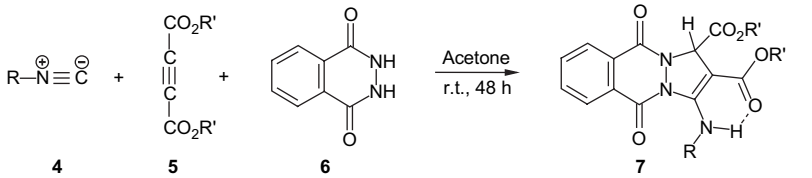
In an extension of our continuing efforts[11i,12a,b,14] on the application of isocyanide-based multicomponent reactions in heterocyclic synthesis, starting with the compounds containing –CH, –NH or –OH acidic group, herein the synthesis of some fused pyrazolophthalazine heterocycles, is reported.

Phthalhydrazide (2,3-dihydro-1,4-phthalazinedione) is a very interesting fused heterobicyclic compound, which has two rather NH-acidic protons.[15] In the present study, this was taken advantage in the formation of the polyfunctional pyrazolophthalazine derivatives incorporating 1*H*-pyrazolo-[1,2-*b*]phthalazine-5,10-dione substructure via a three-component condensation reaction of isocyanides.

2. Results and discussion

The one-pot three-component condensation reactions of alkyl isocyanides **4** with dialkyl acetylenedicarboxylates **5** in the presence of phthalhydrazide **6** proceeded at room temperature in dry acetone and were complete after 48 h to afford corresponding dialkyl 3-(alkylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylates **7**, in moderate to good yields (51–77%). ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of fused pyrazolophthalazine **7**. Any other products could not be detected by NMR spectroscopy. The structures of the products **7a**–**h** were deduced from their elemental analyses and IR, ^{1}H NMR, and ^{13}C NMR spectra (Scheme 2).

The mechanism of this reaction has not been established experimentally, a likely mechanism for the formation of these heterocycles **7** is shown in Scheme 3. In a first step, nucleophilic attack of the isocyanide to the acetylenic ester and subsequent protonation of the highly reactive 1:1 zwitterionic intermediate by NH-acid (phthalhydrazide) affords the vinylisonitrilium cation **8**. Then, vinylisonitrilium cation

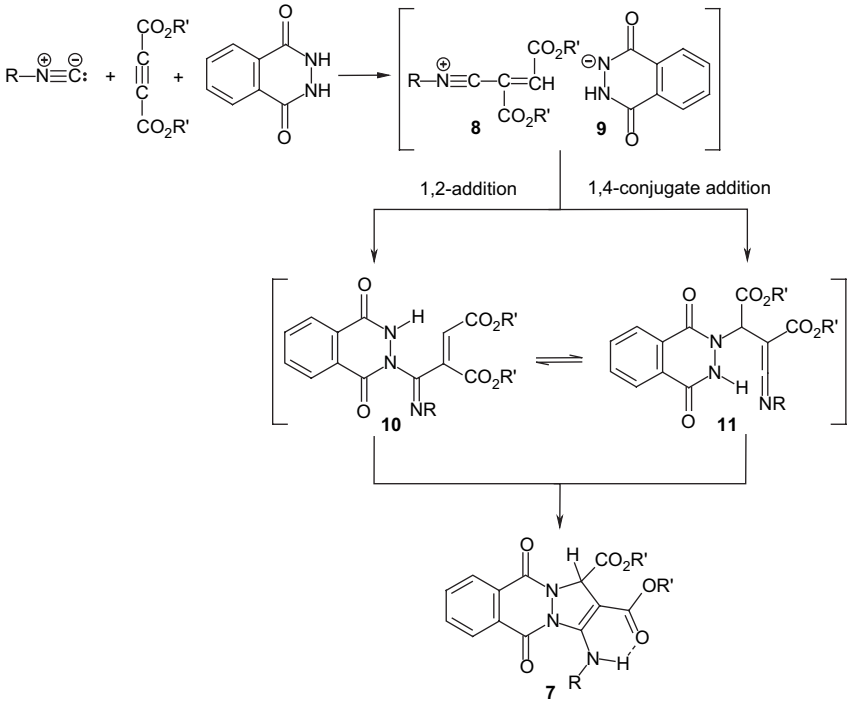


4 **5** **6** **7**

	R	R'
4a	*tert*-Octyl	**5a** Methyl
4b	*tert*-Butyl	**5b** Ethyl
4c	Cyclohexyl	**5c** *tert*-Butyl

	R	R'	Yield (%)
7a	*tert*-Octyl	Methyl	61
7b	*tert*-Butyl	Methyl	57
7c	Cyclohexyl	Methyl	77
7d	*tert*-Octyl	Ethyl	55
7e	*tert*-Butyl	Ethyl	63
7f	Cyclohexyl	Ethyl	69
7g	*tert*-Butyl	*tert*-Butyl	51
7h	Cyclohexyl	*tert*-Butyl	60

Scheme 2.



8 **9** **10** **11** **7**

Scheme 3.

8 could undergo addition reactions with the nitrogen atom of the conjugate base of the NH-acid **9** on the two possible electrophilic sites (1,2-addition and 1,4-conjugate addition) to produce two possible intermediates **10** and **11** in equilibrium with each other. These intermediates can then cyclize under the reaction conditions employed to produce the dialkyl 3-(alkylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylates **7** (Scheme 3).

In summary, the one-pot three-component condensation reaction of alkyl isocyanides with dialkyl acetylenedicarboxylates in presence of phthalhydrazide can be successfully applied to the synthesis of dialkyl 3-(alkylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate derivatives. To the best of our knowledge, this new procedure provides the first example of the efficient synthetic method for 5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate ring systems by formation of three bonds.

3. Experimental

3.1. General

Melting points were measured on a Büchi 535 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN–O-Rapid analyzer. FT-IR Spectra were recorded on a Bruker Equinox-55 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 Avance spectrometer at 400.13 and 100.77 MHz, respectively, with $CDCl_3$ as solvent. The solvents, dimethyl and diethyl acetylenedicarboxylates, cyclohexyl and 1,1,3,3-tetramethylbutyl (*tert*-octyl) isocyanides used in this work were purchased from Merck and the *tert*-butyl isocyanide, and di-*tert*-butylacetylenedicarboxylate were obtained from Fluka (Buchs, Switzerland). The benzyl isocyanide and phthalhydrazide were obtained from Aldrich chemical company. All reagents were used without further purification.

3.2. Typical procedure for preparation of dimethyl 3-[(1,1,3,3-tetramethylbutyl)amino]-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate (7a)

To a magnetically stirred solution of phthalhydrazide (0.081 g, 0.5 mmol) and *tert*-octyl isocyanide (0.070 g, 0.5 mmol) in dry acetone (40 mL) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.071 g, 0.5 mmol) in acetone (2 mL) at room temperature over 10 min via a syringe. The reaction mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the solid residue was washed with diethyl ether and crystallized from CH_2Cl_2/*n*-hexane (1:3) to give **7a** as yellow crystals (0.136 g, 61%).

Mp 239–242°C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3180 (N–H), 1740, 1662 and 1635 (C=O), 1576 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.06 (9H, s, $C(CH_3)_3$), 1.49 and 1.54 (6H, 2s, $C(CH_3)_2$), 1.76 and 2.14 (2H, AB system, $^2J_{HH}$=14.9 Hz, CH_2), 3.74 and 3.79 (6H, 2s, $2OCH_3$), 5.76 (1H, s, NCH), 7.86 and 8.32 (4H, 2m, C_6H_4), 9.04 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 29.01 (C*Me*$_2$), 30.74 (2*C*Me$_3$), 31.65 (C*Me*$_3$), 51.20 (CH_2), 52.94 and 52.96 ($2OCH_3$), 61.23 (*C*Me$_2$), 62.40 (N–CH), 81.00 (*C*=C–N), 127.43, 127.82, 128.22, 129.39, 133.75 and 134.53 (C_6H_4), 149.39 (=*C*–N), 154.21, 158.09, 163.68, 169.77 (4C=O). Anal. Calcd for $C_{23}H_{29}N_3O_6$ (443.49): C, 62.29; H, 6.59; N, 9.47%. Found: C, 62.35; H, 6.65; N, 9.44%.

3.2.1. Dimethyl 3-(*tert*-butylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate (7b). Yellow prisms (0.111 g, 57%); mp 181–183°C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3178 (N–H), 1736, 1711 and 1657 (C=O), 1594 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.52 (9H, s, $C(CH_3)_3$), 3.71 and 3.77 (6H, 2s, $2OCH_3$), 5.69 (1H, s, NCH), 7.84 and 8.32 (4H, 2m, C_6H_4), 8.97 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 29.95 (C*Me*$_3$), 51.42 and 52.96 ($2OCH_3$), 57.54 (*C*Me$_3$), 62.64 (N–CH), 81.87 (*C*=C–N), 127.37, 127.80, 128.25, 129.40, 133.73 and 134.47 (C_6H_4), 149.64 (=*C*–N), 154.50, 157.91, 163.33, 169.14 (4C=O). Anal. Calcd for $C_{19}H_{21}N_3O_6$ (387.38): C, 58.91; H, 5.46; N, 10.85%. Found: C, 59.01; H, 5.44; N, 10.80%.

3.2.2. Dimethyl 3-(cyclohexylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate (7c). Yellow prisms (0.160 g, 77%); mp 171–173°C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3176 (N–H), 1748, 1710 and 1660 (C=O), 1599 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.26–2.06 (10H, m, $5CH_2$), 3.69 and 3.76 (6H, 2s, $2OCH_3$), 4.38 (NHC*H*), 5.66 (1H, s, NCH), 7.83 and 8.27 (4H, 2m, C_6H_4), 8.98 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 24.08, 24.28, 25.49, 33.13 and 33.67 ($5CH_2$), 51.17 and 52.90 ($2OCH_3$), 53.94 (NH–CH), 62.29 (N–CH), 77.92 (*C*=C–N), 127.45, 127.76, 128.20, 129.09, 133.78 and 134.61 (C_6H_4), 149.83 (=*C*–N), 154.09, 157.84, 162.99, 169.93 (4C=O). Anal. Calcd for $C_{21}H_{23}N_3O_6$ (413.42): C, 61.01; H, 5.61; N, 10.16%. Found: C, 59.92; H, 5.60; N, 10.11%.

3.2.3. Diethyl 3-[(1,1,3,3-tetramethylbutyl)amino]-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate (7d). Yellow prisms (0.130 g, 55%); mp 223–225°C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3189 (N–H), 1744, 1668 and 1609 (C=O), 1588 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.08 (9H, s, $C(CH_3)_3$), 1.26 and 1.31 (6H, 2t, $^3J_{HH}$=7.0 Hz, $2OCH_2CH_3$), 1.50 and 1.54 (6H, 2s, $C(CH_3)_2$), 1.77 and 2.12 (2H, AB system, $^2J_{HH}$=15.0 Hz, CH_2), 4.18–4.24 (4H, m, $2ABX_3$ overlapping systems, $2OCH_2CH_3$), 5.86 (1H, s, NCH), 7.88 and 8.32 (4H, 2m, C_6H_4), 8.98 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 14.10 and 14.44 ($2OCH_2CH_3$), 28.97 (C*Me*$_2$), 30.81 (2*C*Me$_3$), 31.70 (C*Me*$_3$), 50.11 (CH_2), 60.02 and 62.21 ($2OCH_2$), 62.23 (*C*Me$_2$), 62.48 (N–CH), 82.23 (*C*=C–N), 127.44, 127.85, 128.41, 129.35, 133.81 and 134.52 (C_6H_4), 149.47 (=*C*–N), 154.90, 159.02, 164.31, 169.80 (4C=O). Anal. Calcd for $C_{25}H_{33}N_3O_6$ (471.55): C, 63.68; H, 7.05; N, 8.91%. Found: C, 63.74; H, 6.99; N, 8.90%.

3.2.4. Diethyl 3-(*tert*-butylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate (7e). Yellow prisms (0.131 g, 63%); mp 232–234°C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3185 (N–H), 1744, 1712 and 1661 (C=O), 1604 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.28 and 1.29 (6H, 2t, $^3J_{HH}$=7.0 Hz, $2OCH_2CH_3$), 1.50 (9H, s,

$C(CH_3)_3$), 4.18–4.24 (4H, m, $2ABX_3$ overlapping systems, $2OCH_2CH_3$), 5.74 (1H, s, NCH), 7.84 and 8.31 (4H, 2m, C_6H_4), 8.77 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 14.12 and 14.43 ($2OCH_2CH_3$), 29.95 (CMe_3), 57.50 (CMe_3), 59.98 and 61.93 ($2OCH_2$), 62.53 (N–CH), 82.27 (C=C–N), 127.42, 127.78, 128.26, 129.40, 133.71 and 134.45 (C_6H_4), 149.74 (=C–N), 154.33, 157.93, 163.29, 169.23 (4C=O). Anal. Calcd for $C_{21}H_{25}N_3O_6$ (415.44): C, 60.71; H, 6.07; N, 10.11%. Found: C, 60.74; H, 6.02; N, 10.08%.

3.2.5. Diethyl 3-(cyclohexylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate (7f). Yellow prisms (0.153 g, 69%); mp 208–210°C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3204 (N–H), 1740, 1708 and 1656 (C=O), 1574 (C=C). ^1H NMR ($CDCl_3$): δ_H 1.26 and 1.31 (6H, 2t, $^3J_{HH}$=7.0 Hz, $2OCH_2CH_3$), 1.28–2.05 (10H, m, $5CH_2$), 4.11–4.25 (4H, m, $2ABX_3$ overlapping systems, $2OCH_2CH_3$), 4.43 (NH–CH), 5.70 (1H, s, NCH), 7.80 and 8.28 (4H, 2m, C_6H_4), 9.01 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 14.14 and 14.42 ($2OCH_2CH_3$), 24.10, 24.28, 25.47, 33.16 and 33.59 ($5CH_2$), 60.18 and 61.90 ($2OCH_2$), 54.01 (NH–CH), 62.40 (N–CH), 79.23 (C=C–N), 127.44, 127.81, 128.23, 128.98, 133.80 and 134.56 (C_6H_4), 149.88 (=C–N), 155.11, 157.81, 163.06, 170.02 (4C=O). Anal. Calcd for $C_{23}H_{27}N_3O_6$ (441.48): C, 62.57; H, 6.16; N, 9.52%. Found: C, 62.60; H, 6.10; N, 9.50%.

3.2.6. Di(*tert*-butyl) 3-(*tert*-butylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate (7g). Yellow prisms (0.121 g, 51%); mp 163–165°C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3171 (N–H), 1743, 1710 and 1651 (C=O), 1589 (C=C). ^1H NMR ($CDCl_3$): δ_H 1.18, 1.25, 1.50 (27H, s, $3C(CH_3)_3$), 5.61 (1H, s, NCH), 7.82 and 8.30 (4H, 2m, C_6H_4), 8.80 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 27.87, 28.11 and 29.86 ($3CMe_3$), 57.56 ($NCMe_3$), 62.60 (N–CH), 79.25 (C=C–N), 127.38, 127.79, 128.31, 129.39, 133.70 and 134.48 (C_6H_4), 148.53 (=C–N), 154.21, 157.84, 164.09, 169.30 (4C=O). Anal. Calcd for $C_{25}H_{33}N_3O_6$ (471.55): C, 63.68; H, 7.05; N, 8.91%. Found: C, 63.74; H, 7.04; N, 8.87%.

3.2.7. Di(*tert*-butyl) 3-(cyclohexylamino)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-1,2-dicarboxylate (7h). Yellow prisms (0.150 g, 60%); mp 199–201°C (dec); IR (KBr) (ν_{max}, cm^{-1}): 3188 (N–H), 1735, 1709 and 1648 (C=O), 1587 (C=C). ^1H NMR ($CDCl_3$): δ_H 1.18–2.04 (10H, m, $5CH_2$), 1.23 and 1.47 (18H, 2s, $2C(CH_3)_3$), 4.40 (NHCH), 5.59 (1H, s, NCH), 7.81 and 8.28 (4H, 2m, C_6H_4), 8.81 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 24.08, 24.28, 25.49, 33.13 and 33.67 ($5CH_2$), 27.15 and 27.26 (CMe_3), 54.12 (NH–CH), 62.36 (N–CH), 81.49 (C=C–N), 81.79 and 84.80 (CMe_3), 127.44, 127.78, 128.23, 129.09, 133.79 and 134.62 (C_6H_4), 149.91 (=C–N), 155.04, 157.88, 162.90, 169.86 (4C=O). Anal. Calcd for $C_{27}H_{35}N_3O_6$ (497.58): C, 65.17; H, 7.09; N, 8.44%. Found: C, 65.23; H, 7.06; N, 8.43%.

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