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Reaction between isocyanides and dialkyl acetylenedicarboxylates in the presence of strong CH-acids: one-pot synthesis of highly functionalized annulated 4*H*-pyrans

Mohammad Bagher Teimouri,[a,*] Reihaneh Bazhrang,[b] Vahid Eslamimanesh[a] and Arezu Nouri[c]

[a]*Petrochemical Department, Iran Polymer and Petrochemical Institute, PO Box 14965-115, Tehran, Iran*
[b]*Biomaterial Department, Iran Polymer and Petrochemical Institute, PO Box 14965-115, Tehran, Iran*
[c]*Central Laboratory, Iran Polymer and Petrochemical Institute, PO Box 14965-115, Tehran, Iran*

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Abstract—The highly reactive 1:1 adduct, produced from the reaction between dialkyl acetylenedicarboxylates and alkyl isocyanides, was trapped by strong cyclic CH-acids such as 4-hydroxy-6-methyl-2*H*-pyran-2-one or 4-hydroxycoumarin to yield dialkyl 2-(alkylamino)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3,4-dicarboxylates or dialkyl 7-methyl-2-(alkylamino)-5-oxo-4*H*,5*H*-pyrano[4,3-*b*]pyran-3,4-dicarboxylates in good yields at room temperature.

1. Introduction

Modern synthetic design demands high efficiency in terms of minimization of synthetic steps together with maximization of complexity.[1] One of the ways to fulfill these goals is the development and use of multicomponent reactions, which consist of several simultaneous bond-forming reactions and allow the highly efficient synthesis of complex molecules starting from simple substrates in a one-pot manner.[2] Multicomponent reactions (MCRs), which can produce a diversity of compounds, provide one of the most efficient methods for the combinatorial synthesis of compound sortiments.[3] Multicomponent reactions can also lead to an increase in molecular complexity by combining a series of reactions in one synthetic operation.[4]

In recent years, isocyanide-based multicomponent condensation reactions (IMCRs) by virtue of their synthetic potential, their inherent atom efficiency, convergent nature, ease of implementation, and the generation of molecular diversity, have attracted much attention because of the advantages that they offer to the field of combinatorial chemistry.[5,6]The fact that complex products can be formed in a single operation by simultaneous reactions of several reagents has caused IMCRs to be among the most powerful methods for the synthesis of organic molecules.[7]

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.[8–11] Recently, these highly reactive zwitterionic intermediates have been captured by suitable CH–,[9] NH–,[10] and OH–acids[11] substrates such as 3-methylcyclopentane-1,2,4-trione,[9d] maleimide[10b] and naphthol,[11a] which produced tetrahydrocyclopenta[*b*]pyrans, 2-aminofuranes and benzochromene derivatives, respectively.

Continuing our interest in isocyanide-based multicomponent reactions,[12] involving electron deficient acetylenic esters,[13] and 4-hydroxycoumarin or 4-hydroxy-6-methyl-2*H*-pyran-2-one[12d,f] we disclose herein three-component reactions, starting from simple and readily available precursors affording products containing highly functionalized annulated 4*H*-pyrans as an expanded paper that includes more results to another report.[9e] Addition of the zwitterionic intermediate generated from alkyl isocyanides **1** and dialkyl acetylenedicarboxylates **2** to 4-hydroxy-6-methyl-2*H*-pyran-2-one or 4-hydroxycoumarin **3** afforded the annulated 4*H*-pyrans **4** in good yields. The reaction can be represented as in Scheme 1.

2. Results and discussion

The one-pot three-component condensation reactions of alkyl isocyanides **1** with dialkyl acetylenedicarboxylates **2** in the presence of 4-hydroxy-6-methyl-2*H*-pyran-2-one or

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* Corresponding author. Tel.: +98 21 44580000; fax: +98 21 44580032; e-mail: m.teimouri@ippi.ac.ir

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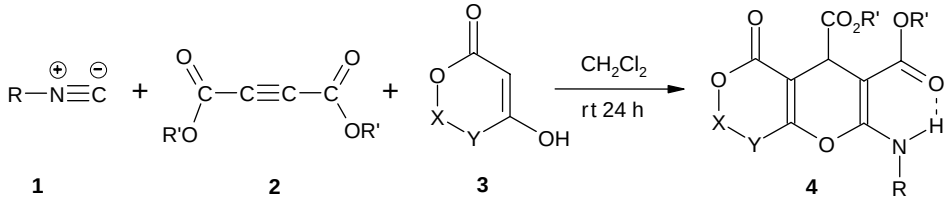


R

1a *tert*-Butyl
1b Cyclohexyl
1c 2-Morpholinoethyl
1d 1,1,3,3-Tetramethylbutyl

R'

2a Methyl
2b Ethyl

X-Y

3a
3b

	X-Y	R'	R	Yield (%)
4a		Methyl	*tert*-Butyl	71
4b		Methyl	Cyclohexyl	64
4c		Methyl	2-Morpholinoethyl	74
4d		Ethyl	Cyclohexyl	62
4e		Ethyl	1,1,3,3-Tetramethylbutyl	58
4f		Methyl	*tert*-Butyl	88
4g		Methyl	Cyclohexyl	78
4h		Methyl	2-Morpholinoethyl	63
4i		Ethyl	*tert*-Butyl	90
4j		Ethyl	1,1,3,3-Tetramethylbutyl	55

Scheme 1.

4-hydroxycoumarin **3** proceeded spontaneously at room temperature in dichloromethane and were complete after 1 day to afford corresponding dialkyl 2-(alkylamino)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3,4-dicarboxylates or dialkyl 7-methyl-2-(alkylamino)-5-oxo-4*H*,5*H*-pyrano-[4,3-*b*]pyran-3,4-dicarboxylates **4**, in moderate to good yields (55–90%). ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of annulated 4*H*-pyrans **4**. No product other than **4** could not be detected by NMR spectroscopy. The structures of the products **4a–j** were deduced from their elemental analyses and IR, ^{1}H and ^{13}C NMR spectra.

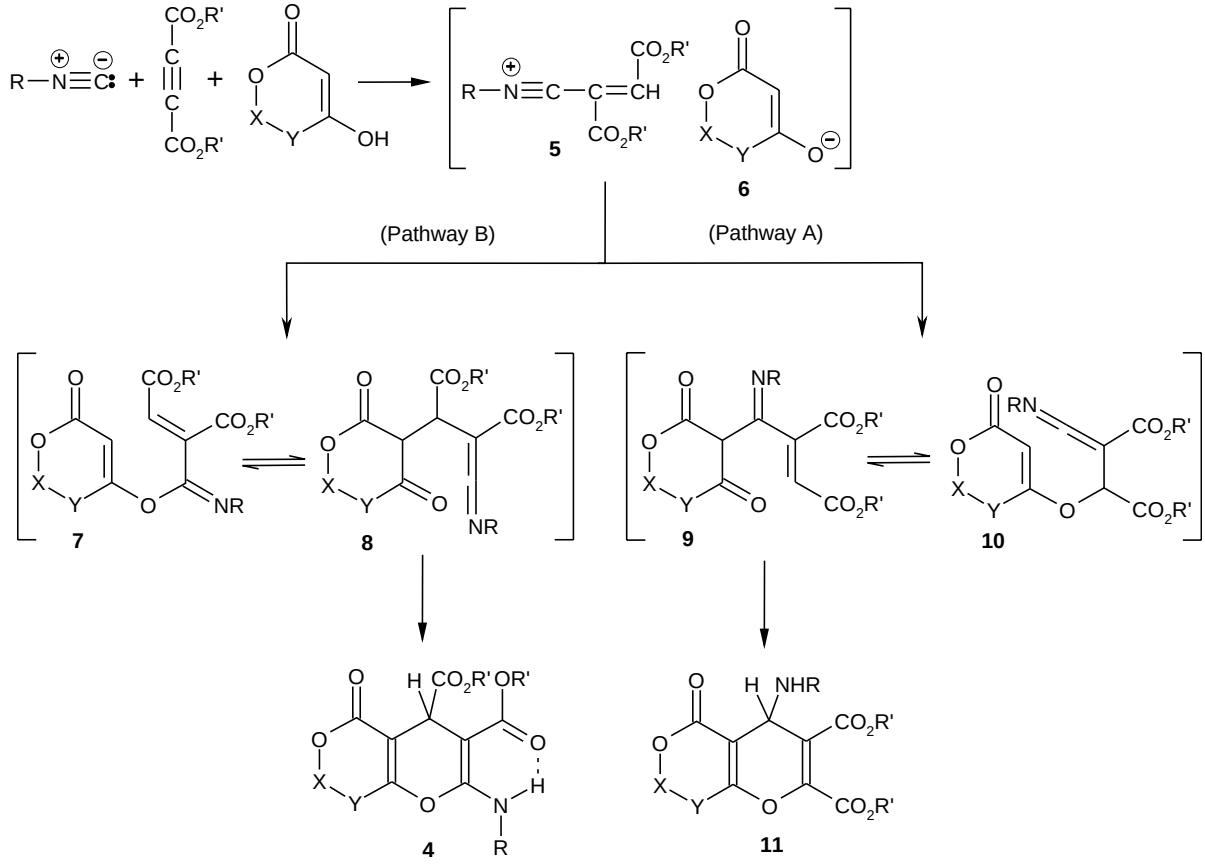
The ^{1}H NMR spectrum of **4a** exhibited six single sharp lines readily recognized as arising from *tert*-butyl (δ 1.40 ppm), methyl (δ 2.25 ppm), two methoxy protons (δ 3.67 and 3.68 ppm), allylic methine (δ 4.54 ppm) and olefinic methine (δ 5.93 ppm). A fairly broad singlet (δ 8.75 ppm) was observed for the NH group. The presence of an amine proton was confirmed by exchange with D_2O. The chemical shift of the NH group indicates that this moiety must have participated in a six-membered intramolecular hydrogen bond formation with the vicinal carbonyl group as shown in Scheme 1.

The ^{1}H decoupled ^{13}C NMR spectrum of **4a** showed 15 distinct resonances in agreement with the suggested structure. Partial assignment of these resonances is given in Section 3.

The structural assignments made on the basis of the ^{1}H and ^{13}C NMR spectra of compounds **4a** was supported by measurement of its IR spectra. The IR spectrum of **4a** showed strong absorptions at 1724, 1676 and 1615 cm^{-1} due to the carbonyls and the amino group at 3220 cm^{-1} as a weak broad band.

The ^{1}H and ^{13}C NMR spectra of **4b–j** are similar to those of **4a** and the results are summarized in Section 3. Although the mechanism of this reaction has not been established experimentally, the formation of these heterocycles can be rationalized by initial Michael-type addition[14] of the isocyanide to the acetylenic ester and subsequent protonation of the highly reactive 1:1 zwitterionic intermediate by strong CH-acid leads to vinylisonitrilium cation **5**, which could have undergone addition reactions with bidentate enolate anion **6** on two possible electrophilic sites to produce four possible intermediates **7–10**. Adducts **7** and **8**, as well as, **9** and **10** can be interconverted by Claisen rearrangement. Intermediates **8** and **9** can be cyclized under the reaction conditions employed to produce the annulated 4*H*-pyrans **4** and **11**, respectively (Scheme 2). Since the ^{1}H NMR signal of the allylic saturated methine proton exhibited a sharp singlet in different solvents, the structure **11**, which is expected to show vicinal coupling for the HC–NH moiety, is excluded. Moreover, the ^{1}H and ^{13}C chemical shifts of the allylic methine group are in better agreement with the structure **4**. Interestingly, it has been found that this reaction is highly chemoselective in the preparation of fused heterocyclic enaminoester **4**, since no other detectable product is formed under the described reaction conditions.

In conclusion, we have found that the one-pot three-component chemoselective reaction of isocyanides, with



Scheme 2.

dialkyl acetylenedicarboxylate in the presence of relatively strong cyclic CH-acids such as 4-hydroxy-6-methyl-2*H*-pyran-2-one or 4-hydroxycoumarin leads to a facile synthesis of highly functionalized dialkyl 2-(alkylamino)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3,4-dicarboxylates or dialkyl 7-methyl-2-(alkylamino)-5-oxo-4*H*,5*H*-pyrano-[4,3-*b*]pyran-3,4-dicarboxylates **4** in good yields, respectively. The present method has advantages that, not only the reaction is performed under neutral conditions, but the substances can be mixed without any activation or modification.

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. IR Spectra were recorded on a Shimadzu IR-470 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. NMR spectra were obtained by solutions made in $CDCl_3$. The solvents, strong CH-acids, dialkyl acetylenedicarboxylates, cyclohexyl and 1,1,3,3-tetramethylbutyl isocyanides used in this work were purchased from Merck and the *tert*-butyl and 2-morpholinoethyl isocyanides were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

3.1.1. Typical procedure for preparation of dimethyl 7-methyl-2-(*tert*-butylamino)-5-oxo-4*H*,5*H*-pyrano[4,3-*b*]-pyran-3,4-dicarboxylate (4a). To a magnetically stirred solution of 4-hydroxy-6-methyl-2*H*-pyran-2-one (0.127 g, 1.0 mmol) and dimethyl acetylenedicarboxylate (0.143 g, 1.0 mmol) in dichloromethane (40 mL) was added dropwise a mixture of *tert*-butyl isocyanide (0.084 g, 1.0 mmol) in dichloromethane (10 mL) at room temperature over 10 min via a syringe. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum and the solid residue was washed with diethyl ether and crystallized from CH_2Cl_2–*n*-hexane (1/2) to give **4a** as white crystals (0.250 g, 71%); mp 183–185 °C; IR (KBr) (ν_{max}, cm^{-1}): 3220 (N–H), 1724, 1676 and 1615 (C=O), 1604 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.40 (9H, s, $C(CH_3)_3$), 2.25 (3H, s, =C—CH_3), 3.67 and 3.68 (6H, 2s, $2OCH_3$), 4.54 (1H, s, CH), 5.93 (1H, s, =CH), 8.76 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 20.02 (CH_3), 30.55 ($2CMe_3$), 35.52 (CH), 51.17 (CMe_3), 52.56 and 52.89 ($2OCH_3$), 72.95 (*C*=C–N), 98.16 (*C*H=C—CH_3), 99.86 (C=*C*–CH), 159.04, 159.69, 162.41, 162.76, 169.43 and 173.29 (3C=O, 2O–*C*=C and =*C*–N). Anal. Calcd for $C_{17}H_{21}NO_7$ (351.35): C, 58.11; H, 6.02; N, 3.99%. Found: C, 58.20; H, 5.96; N, 3.95%.

3.1.2. Dimethyl 7-methyl-2-(cyclohexylamino)-5-oxo-4*H*,5*H*-pyrano[4,3-*b*]pyran-3,4-dicarboxylate (4b). Cream crystals (0.242 g, 64%); mp 118–120 °C; IR (KBr) (ν_{max}, cm^{-1}): 3245 (N–H), 1719, 1682 and 1612 (C=O), 1603 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.24–2.18 (10H, m,

5CH_2), 2.23 (3H, s, =C—CH_3), 3.66 and 3.67 (6H, 2s, 2OCH_3), 3.75 (1H, m, N–CH), 4.51 (1H, s, CH), 5.93 (1H, s, =CH), 8.61 (1H, d, $^3J_{HH}$=6.2 Hz, NH···O=C). ^{13}C NMR ($CDCl_3$, Me_4Si): δ_C 19.99 (CH_3), 24.41, 25.36, 32.10, 33.50 and 33.77 (5CH_2), 35.71 (CH), 50.13 (N–CH), 51.10 and 52.56 (2OCH_3), 72.00 (*C*=C–N), 98.33 (*C*H=C—CH_3), 99.80 (C=*C*–CH), 158.34, 159.73, 162.49, 162.63, 169.35 and 173.48 (3C=O, 2O–*C*=C and =*C*–N). Anal. Calcd for $C_{19}H_{23}NO_7$ (377.38): C, 60.47; H, 6.14; N, 3.71%. Found: C, 60.55; H, 6.20; N, 3.69%.

3.1.3. Dimethyl 7-methyl-2-[(2-morpholinoethyl)amino]-5-oxo-4*H*,5*H*-pyrano[4,3-*b*]pyran-3,4-dicarboxylate (4c). Cream crystals (0.303 g, 74%); mp 154–156 °C; IR (KBr) (ν_{max}, cm^{-1}): 3220 (N–H), 1722, 1687 and 1662 (C=O), 1619 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 2.23 (3H, s, =C—CH_3), 2.49 (4H, m, CH_2NCH_2), 2.55 (2H, t, $^3J_{HH}$= 5.6 Hz, NCH_2), 3.45 (2H, d of t, $^3J_{HH}$=5.6, 5.0 Hz, NHCH_2), 3.66 and 3.67 (6H, 2s, 2OCH_3), 3.71 (4H, m, CH_2OCH_2), 4.51 (1H, s, CH), 5.92 (1H, s, =CH), 8.73 (1H, t, $^3J_{HH}$=5.0 Hz, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 20.02 (CH_3), 35.81 ($NHCH_2$), 37.76 (CH), 51.15 and 52.56 (2OCH_3), 53.37 (CH_2NCH_2), 57.34 (NCH_2), 66.80 (CH_2OCH_2), 72.77 (*C*=C–N), 98.21 (*C*H=C—CH_3), 99.79 (C=*C*–CH), 158.56, 159.24, 162.37, 162.66, 169.00 and 173.46 (3C=O, 2O–*C*=C and =*C*–N). Anal. Calcd for $C_{19}H_{24}N_2O_8$ (408.40): C, 55.88; H, 5.92; N, 6.86%. Found: C, 56.00; H, 6.01; N, 6.83%.

3.1.4. Diethyl 7-methyl-2-(cyclohexylamino)-5-oxo-4*H*,5*H*-pyrano[4,3-*b*]pyran-3,4-dicarboxylate (4d). Cream crystals (0.252 g, 62%); mp 139–141 °C; IR (KBr) (ν_{max}, cm^{-1}): 3260 (N–H), 1730, 1680 and 1636 (C=O), 1609 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.22–2.21 (10H, m, 5CH_2), 1.24 and 1.25 (6H, 2t, $^3J_{HH}$=7.0 Hz, 2OCH_2CH_3), 2.24 (3H, s, =C—CH_3), 3.63 (1H, m, N–CH), 4.08–4.25 (4H, m, 2ABX_3 overlapping systems, 2O*C*$H_2$$CH_3$), 4.52 (1H, s, CH), 5.93 (1H, s, =CH), 8.65 (1H, br s, NH··· O=C). ^{13}C NMR ($CDCl_3$): δ_C 14.18 and 14.43 (2OCH_2CH_3), 19.97 (CH_3), 24.45, 25.39, 32.36, 33.53 and 33.81 (5CH_2), 35.97 (CH), 50.12 (N–CH), 59.74 and 61.29 (2OCH_2), 72.18 (*C*=C–N), 98.35 (*C*H=C—CH_3), 99.90 (C=*C*–CH), 158.25, 159.36, 162.49, 162.57, 169.07 and 173.37 (3C=O, 2O–*C*=C and =*C*–N). Anal. Calcd for $C_{21}H_{27}NO_7$ (405.44): C, 62.21; H, 6.71; N, 3.45%. Found: C, 60.24; H, 6.65; N, 3.49%.

3.1.5. Diethyl 7-methyl-2-[(1,1,3,3-tetramethylbutyl)-amino]-5-oxo-4*H*,5*H*-pyrano[4,3-*b*]pyran-3,4-dicarboxylate (4e). White crystals (0.253 g, 58%); mp 120–122 °C; IR (KBr) (ν_{max}, cm^{-1}): 3231 (N–H), 1733, 1680 and 1648 (C=O), 1606 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 0.97 (9H, s, $C(CH_3)_3$), 1.22 and 1.24 (6H, 2t, $^3J_{HH}$=7.1 Hz, 2OCH_2CH_3), 1.42 and 1.43 (6H, 2s, $C(CH_3)_2$), 1.69 (2H, s, CH_2), 2.25 (3H, s, =C—CH_3), 4.08–4.18 (4H, m, 2ABX_3 overlapping systems, 2O*C*$H_2$$CH_3$), 4.53 (1H, s, CH), 5.91 (1H, s, =CH), 8.83 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 14.16 and 14.41 (2OCH_2CH_3), 20.01 (CH_3), 31.22 (*C*Me_3), 31.42 (C*Me*$_3$), 31.66 (C*Me*$_2$), 35.80 (CH), 53.57 (CH_2), 56.37 (*C*Me_2), 59.76 and 61.24 (2OCH_2), 72.76 (*C*=C–N), 98.13 (*C*H=C—CH_3), 99.97 (C=*C*–CH), 159.00, 159.44, 162.51, 162.71, 169.13 and 173.05 (3C=O, 2O–*C*=C and =*C*–N). Anal. Calcd for $C_{23}H_{33}NO_7$ (435.51): C, 63.43; H, 7.64; N, 3.22%. Found: C, 63.50; H, 7.59; N, 3.25%.

3.1.6. Dimethyl 2-(*tert*-butylamino)-5-oxo-4*H*,5*H*-pyrano-[3,2-*c*]chromene-3,4-dicarboxylate (4f). Pale yellow crystals (0.341 g, 88%); mp 214–216 °C; IR (KBr) (ν_{max}, cm^{-1}): 3225 (N–H), 1726, 1681 and 1643 (C=O), 1607 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.53 (9H, s, $C(CH_3)_3$), 3.69 and 3.73 (6H, 2s, 2OCH_3), 4.73 (1H, s, CH), 7.35–7.84 (4H, m, arom.), 8.99 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 30.55 (2C*Me*$_3$), 36.11 (CH), 51.24 (*C*Me_3), 52.61 and 52.85 (2OCH_3), 72.88 (*C*=C–N), 103.04 (=*C*–CH), 113.50, 117.17, 122.32, 124.32, 132.68 and 152.71 (six arom. carbons), 154.97 (*C*=C–CH), 159.55, 160.64, 169.43 and 172.94 (3C=O and =*C*–N). Anal. Calcd for $C_{20}H_{21}NO_7$ (387.38): C, 62.01; H, 5.46; N, 3.62%. Found: C, 61.90; H, 5.40; N, 3.66%.

3.1.7. Dimethyl 2-(cyclohexylamino)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3,4-dicarboxylate (4g). White crystals (0.323 g, 78%); mp 199–201 °C; IR (KBr) (ν_{max}, cm^{-1}): 3250 (N–H), 1731, 1690 and 1662 (C=O), 1603 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.14–2.05 (10H, m, 5CH_2), 3.66 and 3.70 (6H, 2s, 2OCH_3), 3.84 (1H, m, N–CH), 4.68 (1H, s, CH), 7.22–7.79 (4H, m, arom.), 8.68 (1H, br s, NH··· O=C). ^{13}C NMR ($CDCl_3$, Me_4Si): δ_C 24.45, 25.39, 32.05, 33.46 and 33.73 (5CH_2), 36.30 (CH), 50.65 (N–CH), 51.20 and 52.67 (2OCH_3), 72.13 (*C*=C–N), 102.97 (=*C*–CH), 113.59, 117.08, 121.94, 124.62, 132.47 and 152.75 (six arom. carbons), 154.89 (*C*=C–CH), 158.26, 160.67, 169.30 and 173.09 (3C=O and =*C*–N). Anal. Calcd for $C_{22}H_{23}NO_7$ (413.42): C, 63.91; H, 5.61; N, 3.39%. Found: C, 64.02; H, 5.65; N, 3.44%.

3.1.8. Dimethyl 2-[(2-morpholinoethyl)amino]-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3,4-dicarboxylate (4h). Cream crystals (0.280 g, 63%); mp 218–220 °C; IR (KBr) (ν_{max}, cm^{-1}): 3195 (N–H), 1730, 1679, 1644 (C=O), 1607 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 2.51 (4H, m, CH_2NCH_2), 2.63 (2H, t, $^3J_{HH}$=5.1 Hz, NCH_2), 3.63 (2H, d of t, $^3J_{HH}$= 5.1, 4.3 Hz, NHCH_2), 3.67 and 3.71 (6H, 2s, 2OCH_3), 3.72 (4H, m, CH_2OCH_2), 4.68 (1H, s, CH), 6.87–7.75 (4H, m, arom.), 8.81 (1H, t, $^3J_{HH}$=4.3 Hz, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 36.43 ($NHCH_2$), 38.13 (CH), 51.24 and 52.68 (2OCH_3), 53.40 (CH_2NCH_2), 57.16 (NCH_2), 66.88 (CH_2OCH_2), 72.78 (*C*=C–N), 102.96 (=*C*–CH), 113.49, 117.06, 122.11, 124.51, 132.77 and 152.72 (six arom. carbons), 154.81 (*C*=C–CH), 158.47, 160.61, 168.91 and 173.10 (3C=O and =*C*–N). Anal. Calcd for $C_{22}H_{24}N_2O_8$ (444.43): C, 59.45; H, 5.44; N, 6.30%. Found: C, 59.54; H, 5.40; N, 6.26%.

3.1.9. Diethyl 2-(*tert*-butylamino)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3,4-dicarboxylate (4i). White crystals (0.374 g, 90%); mp 192–194 °C; IR (KBr) (ν_{max}, cm^{-1}): 3231 (N–H), 1732, 1684 and 1644 (C=O), 1601 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 1.23 and 1.28 (6H, 2t, $^3J_{HH}$=7.1 Hz, 2OCH_2CH_3), 1.52 (9H, s, $C(CH_3)_3$), 4.11–4.22 (4H, m, 2ABX_3 overlapping systems, 2O*C*$H_2$$CH_3$), 4.71 (1H, s, CH), 7.34–7.83 (4H, m, arom.), 9.01 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 14.16 and 14.46 (2CH_3), 30.60 (2C*Me*$_3$), 36.41 (CH), 51.81 (*C*Me_3), 59.98 and 61.47 (2OCH_2), 73.06 (*C*=C–N),

103.16 (=*C*–CH), 113.62, 117.22, 122.37, 124.61, 132.63 and 152.76 (six arom. carbons), 155.06 (*C*=C–CH), 159.48, 160.85, 169.19 and 172.99 (3C=O and =*C*–N). Anal. Calcd for $C_{22}H_{25}NO_7$ (415.43): C, 63.61; H, 6.07; N, 3.37%. Found: C, 63.54; H, 6.04; N, 3.40%.

3.1.10. Diethyl 2-[(1,1,3,3-tetramethylbutyl)amino]-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3,4-dicarboxylate (4j). White crystals (0.260 g, 55%); mp 152–154 °C; 3225 (N–H), 1728, 1676 and 1654 (C=O), 1600 (C=C). ^{1}H NMR ($CDCl_3$): δ_H 0.98 (9H, s, $C(CH_3)_3$), 1.23 and 1.28 (6H, 2t, $^3J_{HH}$=7.1 Hz, $2OCH_2CH_3$), 1.54 and 1.57 (6H, 2s, $C(CH_3)_2$), 1.87 (2H, s, CH_2), 4.09–4.23 (4H, m, $2ABX_3$ overlapping systems, $2OCH_2CH_3$), 4.71 (1H, s, CH), 7.35–7.86 (4H, m, arom.), 9.09 (1H, br s, NH···O=C). ^{13}C NMR ($CDCl_3$): δ_C 14.16 and 14.44 ($2OCH_2CH_3$), 31.18 (CMe_3), 31.42 (CMe_3), 31.57 and 31.74 (CMe_2), 36.43 (CH), 53.48 (CH_2), 56.43 (CMe_2), 59.94 and 61.42 ($2OCH_2$), 72.74 (*C*=C–N), 103.28 (=*C*–CH), 113.61, 117.27, 122.38, 124.58, 132.62 and 152.78 (six arom. carbons), 155.07 (*C*=C–CH), 159.43, 160.83, 169.24 and 172.86 (3C=O and =*C*–N). Anal. Calcd for $C_{26}H_{33}NO_7$ (471.54): C, 66.23; H, 7.05; N, 2.97%. Found: C, 66.28; H, 7.00; N, 3.01%.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2006.01.039.

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