PERKIN 1 COMMUNICATION

Reaction between isocyanides and dialkyl acetylenedicarboxylates in the presence of 3-methylcyclopentane-1,2,4-trione. One-pot diastereoselective synthesis of tetrahydrocyclopenta[*b*]pyran derivatives

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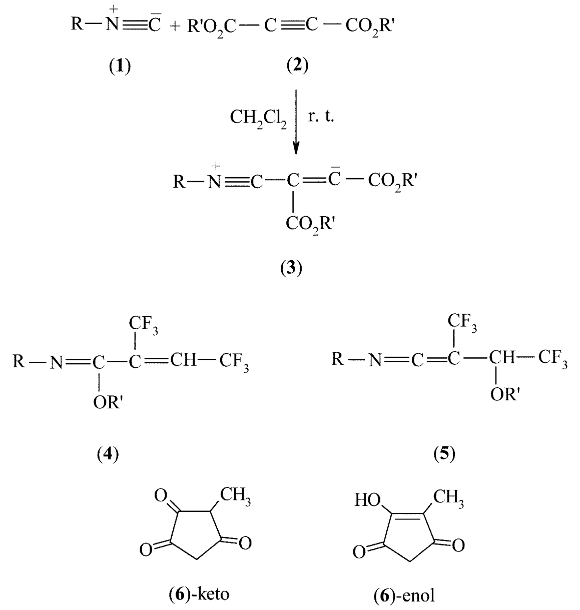
Received (in Cambridge, UK) 1st August 2002, Accepted 23rd September 2002
First published as an Advance Article on the web 3rd October 2002

The reactive 1 : 1 intermediate produced in the reaction between alkyl or aryl isocyanides and dialkyl acetylenedicarboxylates was trapped by 3-methylcyclopentane-1,2,4-trione to yield highly functionalized tetrahydrocyclopenta[*b*]pyran derivatives in excellent yields.

Introduction

The reaction of isocyanides **1** with carbon-centered triple bonds tends to occur in a stepwise manner through a zwitterionic intermediate, the ultimate fate of which appears to be dictated by the nature of the original triple-bonded substrate.[1–4] In the case of electron-deficient acetylenic esters **2**, it is reasonable to assume the prior formation of a 1 : 1 intermediate **3** which possesses predominately carbanionic character (Scheme 1).



Scheme 1

In order to confirm the presence of the highly reactive intermediate **3**, the reaction was carried out with various olefins as solvents, but produced the same products as obtained in the absence of any olefin.[5] However, the existence of the 1 : 1 intermediate was indicated by the isolation of two different 1 : 1 : 1 adducts, *viz.* an amino ester **4** and a ketenimine **5**, from the reaction mixture of an isocyanide with hexafluorobut-2-yne in the presence of an alcohol (Scheme 1).[6,7]

The work reported here was undertaken in order to study the possibility of trapping the reactive 1 : 1 intermediate **3** using a strong CH-acid such as 3-methylcyclopentane-1,2,4-trione **6**. Compound **6** is a readily available[8] multifunctional system, which is apparently completely enolized in the liquid phase, as indicated by ^{1}H and ^{13}C NMR spectroscopy (Scheme 1).

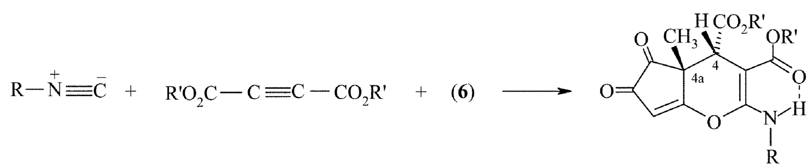
Results and discussion

Alkyl or aryl isocyanides **1** and acetylenic esters **2** in the presence of compound **6** undergo a smooth 1 : 1 : 1 addition reaction in dichloromethane at room temperature, to produce 4a-methyl-5,6-dioxo-4,4a,5,6-tetrahydrocyclopenta[*b*]pyran derivatives **7** in excellent yields (Scheme 2). ^{1}H and ^{13}C NMR spectra of the crude mixture clearly indicate the formation of the products. The structures of compounds **7a**–**h** were deduced from their elemental analyses and their IR, ^{1}H and ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks, any initial fragmentation involved the loss of ester moieties.

The ^{1}H NMR spectrum of **7a** exhibited six sharp lines readily recognized as arising from methyl (δ 1.36), *tert*-butyl (δ 1.42), methoxy (δ 3.55 and 3.73), methine (δ 3.99) and vinylic (δ 6.37) protons. A fairly broad singlet (δ 8.96) is observed for the NH group. The proton decoupled ^{13}C NMR spectrum of **7a** showed 15 distinct resonances in agreement with the proposed structure. Partial assignment of these resonances is given in the Experimental section. The stereochemical relationship of the methyl group and the adjacent hydrogen atom was established by differential nuclear Overhauser effect measurment.[9–11] Thus, when the methyl group of **7a** was irradiated, the differential NOE for its adjacent proton at δ = 3.99 was more than ten times higher than that of the methoxy signal at δ = 3.73. Thus, the methyl group and its adjacent hydrogen atom are in a *syn* conformation. Since, the reaction is stereoselective and leads to one diastereoisomer, namely 4*S*, 4a*R* (or 4*R*, 4a*S*), our attempts to detect the second diastereoisomer in the reaction mixture were not successful.

The ^{1}H and ^{13}C NMR spectra of compounds **7b**–**i** are similar to those of **7a** except for the alkylamino and ester groups, which exhibit characteristic signals with appropriate chemical shifts (see Experimental section).

Although we have not established the mechanism of the reaction between isocyanides and acetylenic esters in the presence of compound **6** in an experimental manner, a possible explanation is proposed in Scheme 3. The first step involves addition of the isocyanide to the acetylenic ester and subsequent protonation of the 1 : 1 adduct **3** by compound **6**. Two possible electrophilic sites are available on **8** for the attacking bidentate anion of **6**. Thus, four adducts **9**–**12** can be considered as possible intermediates. Structures **9** and **10**, as well as, **11** and **12** can be interconverted by Claisen rearrangement (see Scheme 3). Intermediates **10** and **12** can isomerize under the reaction conditions employed to produce the fused heterocyclic systems **7** and **13**, respectively. Since the ^{1}H NMR signal of the saturated methine group exhibits a sharp singlet in differ-

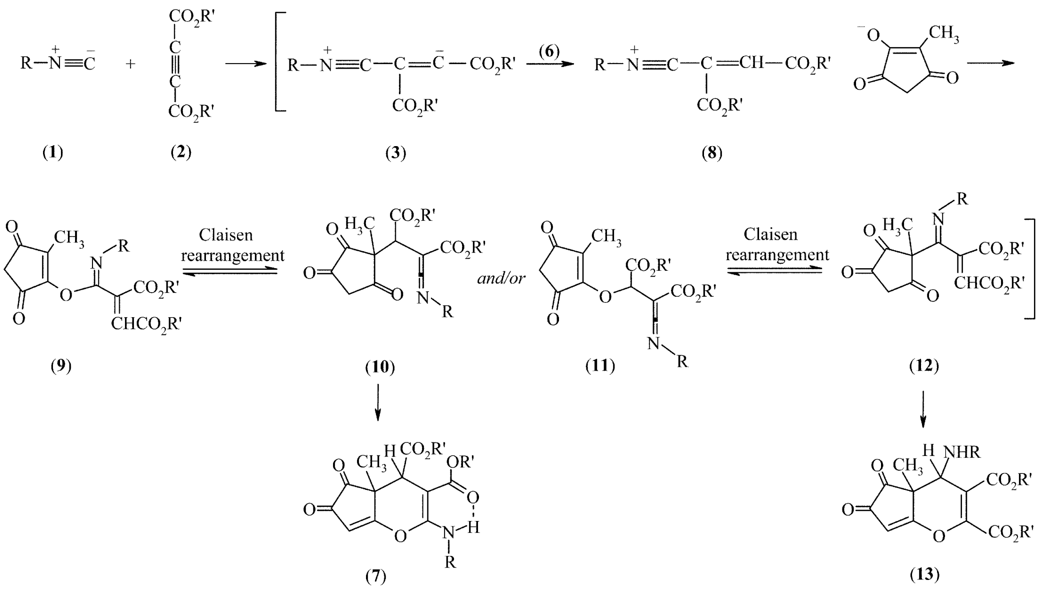


(1)	R
a	^{t}Bu
b	Cyclohexyl
c	2,6-$Me_2C_6H_3$

(2)	R′
a	Me
b	Et
c	^{t}Bu

(7)	R	R′	% Yield
a	^{t}Bu	Me	94
b	^{t}Bu	Et	95
c	^{t}Bu	^{t}Bu	90
d	Cyclohexyl	Me	95
e	Cyclohexyl	Et	95
f	2,6-$Me_2C_6H_3$	Me	92
g	2,6-$Me_2C_6H_3$	Et	90
h	2,6-$Me_2C_6H_3$	^{t}Bu	85

Scheme 2



Scheme 3

ent solvents, we exclude structure **13**, which is expected to show vicinal coupling for the HC–NH moiety. Moreover, the ^1H and ^{13}C chemical shifts of the methine group are in better agreement with the enaminoester **7**.

In summary, the reaction between alkyl or aryl isocyanides and dialkyl acetylenedicarboxylates in the presence of 3-methylcyclopentane-1,2,4-trione provides a simple one-pot entry into the stereoselective synthesis of polyfunctional tetrahydrocyclopenta[*b*]pyran derivatives of potential synthetic interest. The present method has the advantage of being performed under neutral conditions and requiring no activation or modification of the adducts.

Experimental

Dialkyl acetylenedicarboxylates, *tert*-butyl isocyanide, 2,6-dimethylphenyl isocyanide and cyclohexyl isocyanide were obtained from Fluka (Buchs, Switzerland) and were used without further purification. 3-Methylcyclopentane-1,2,3-trione was prepared according to literature.[8] Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 70 eV. ^1H and ^{13}C NMR spectra were measured ($CDCl_3$ solution) with a Brucker DRX-500 AVANCE spectrometer at 500.1 and 125.8 MHz, respectively. IR spectra were recorded on a Shimadzu IR-460 spectrometer. Chromatography columns were prepared from Aldrich silica gel 70–230 mesh.

General procedure

To a magnetically stirred solution of 3-methylcyclopentane-1,2,4-trione (0.126 g, 1 mmol) and the appropriate acetylenedicarboxylate (1 mmol) in dichloromethane (6 mL) was added dropwise a mixture of the appropriate isocyanide (1 mmol) in dichloromethane (2 mL) at −5 °C for 10 min. The reaction mixture was then allowed to warm up to room temperature and was stirred for 24 h. The solvent was removed under reduced pressure and the product was purified by column chromatography using hexane–ethyl acetate (2 : 1) as eluent. The solvent was removed under reduced pressure and the product was obtained.

Dimethyl 2-(*tert*-butylamino)-4a-methyl-5,6-dioxo-4,4a,5,6-tetrahydrocyclopenta[*b*]pyran-3,4-dicarboxylate (7a)

Yellow crystals, mp 153–154 °C (from 1 : 1 hexane–ethyl acetate), 0.33 g, yield 94%. IR (KBr) (υ_{max}/cm^{-1}): 3245 (NH), 1766, 1710 and 1660 (C=O). MS, *m*/*z* (%): 351 (M^+, 10), 292 (15), 264 (100), 227 (15), 204 (18), 105 (6), 80 (10), 59 (8). Anal.

calcd for $C_{17}H_{21}NO_7$ (351.36): C, 58.11; H, 6.02; N, 3.99. Found: C, 58.1; H, 6.1; N, 4.0%. ^{1}H NMR: δ 1.36 (3 H, s, CH_3), 1.42 [9 H, s, $C(CH_3)_3$], 3.55 and 3.73 (6 H, 2 s, 2 OCH_3), 3.99 (1 H, s, CH), 6.37 (1 H, s, O–C=CH), 8.96 (1 H, br s, NH). ^{13}C NMR: δ 21.37 (C–*C*H_3), 30.52 [C(*C*H_3)$_3$], 42.00 (*C*HCO_2CH_3), 42.86 (*C*–CH_3), 51.56 and 52.66 (2 OCH_3), 53.59 [*C*(CH_3)$_3$], 73.22 (O–C=*C*), 113.33 (O–C=*C*H), 158.74 (C), 169.42 and 172.14 (2 C=O, ester), 181.28 (C), 185.96 and 197.04 (2 C=O).

Diethyl 2-(*tert*-butylamino)-4a-methyl-5,6-dioxo-4,4a,5,6-tetrahydrocyclopenta[*b*]pyran-3,4-dicarboxylate (7b)

Pale yellow crystals, mp 98–100 °C (from 2 : 1 hexane–ethyl acetate), 0.36 g, yield 95%. IR (KBr) (υ_{max}/cm^{-1}): 3285 (NH), 1761, 1714 and 1662 (C=O). MS, *m*/*z* (%): 379 (M$^+$, 18), 306 (13), 278 (100), 255 (60), 204 (21), 105 (15), 80 (12), 73 (35). Anal. calcd for $C_{19}H_{25}NO_7$ (379.41): C, 60.15; H, 6.64; N, 3.69. Found: C, 60.1; H, 6.6; N, 3.7%. ^{1}H NMR: δ 1.09 and 1.23 (6 H, 2 t, *J*=7.1 Hz, 2 CH_2C*H*$_3$), 1.32 (3 H, s, CH_3), 1.38 [9 H, s, $C(CH_3)_3$], 3.94 (2 H, 2 dq, AMX_3 system, ^2J=10.8 Hz and ^3J=7.1 Hz, OC*H*$_2$$CH_3$), 3.95 (1 H, s, CH), 4.13 (2 H, 2 dq, AMX_3 system, ^2J=10.7 Hz and ^3J=7.1 Hz, OC*H*$_2$$CH_3$), 6.31 (1 H, s, O–C=CH), 8.92 (1 H, br s, NH). ^{13}C NMR: δ 13.84 and 14.36 (2 OCH_2*C*H_3), 21.41 (C–*C*H_3), 30.47 [C(*C*H_3)$_3$], 42.12 (*C*H$CO_2CH_2CH_3$), 42.82 (*C*–CH_3), 53.44 [*C*(CH_3)$_3$], 61.50 and 61.55 (2 O*C*H_2CH_3), 73.49 (O–C=*C*), 113.22 (O–C=*C*H), 158.65 (C), 169.00 and 171.59 (2 C=O, ester), 181.46 (C), 185.95 and 197.26 (2 C=O).

Di-*tert*-butyl 2-(*tert*-butylamino)-4a-methyl-5,6-dioxo-4,4a,5,6-tetrahydrocyclopenta[*b*]pyran-3,4-dicarboxylate (7c)

Yellow crystals, mp 178–180 °C (from 2 : 1 hexane–ethyl acetate), 0.39 g, yield 90%. IR (KBr) (υ_{max}/cm^{-1}): 3230 (NH), 1766, 1708, 1659, 1598 (C=O). MS, *m*/*z* (%): 435 (M$^+$, 6), 348 (8), 320 (45), 311 (15), 232 (25), 105 (10), 87 (35), 57 (100). Anal. calcd for $C_{23}H_{33}NO_7$ (435.52): C, 73.20; H, 8.81; N, 3.71. Found: C, 73.2; H, 8.8; N, 3.7%. ^{1}H NMR: δ 1.32 [9 H, s, $NC(CH_3)_3$], 1.36 (3 H, s, CH_3), 1.43 and 1.45 [18 H, 2 s, 2 $OC(CH_3)_3$], 3.80 (1 H, s, CH), 6.35 (1 H, s, O–C=CH), 8.90 (1 H, br s, NH). ^{13}C NMR: δ 21.73 (C–*C*H_3), 27.88 and 28.51 [2 OC(*C*H_3)$_3$], 30.63 [NC(*C*H_3)$_3$], 43.28 (*C*CH_3), 43.50 [*C*H$CO_2C(CH_3)_3$], 53.28 [N*C*(CH_3)$_3$], 75.28 (O–C=*C*), 80.34 and 82.34 [2 O*C*(CH_3)$_3$], 113.03 (O–C=*C*H), 158.48 (C), 168.72 and 170.92 (2 C=O, ester), 182.55 (C), 186.20 and 197.83 (2 C=O).

Dimethyl 2-(cyclohexylamino)-4a-methyl-5,6-dioxo-4,4a,5,6-tetrahydrocyclopenta[*b*]pyran-3,4-dicarboxylate (7d)

Pale yellow crystals, mp 78–81 °C (from 2 : 1 hexane–ethyl acetate), 0.36 g, yield 95%. IR (KBr) (υ_{max}/cm^{-1}): 3235 (NH), 1762, 1713, 1665, 1600 (C=O). MS, *m*/*z* (%): 377 (M$^+$, 11), 320 (23), 292 (100), 253 (35), 232 (20), 105 (15), 80 (10), 59 (8), 28 (55). Anal. calcd for $C_{19}H_{23}NO_7$ (377.39): C, 60.47; H, 6.14; N, 3.71. Found: C, 60.5; H, 6.2; N, 3.7%. ^{1}H NMR: δ 1.29 (3 H, s, CH_3), 1.52–1.92 (10 H, m, CH(C*H*$_2$)$_5$), 3.49 and 3.69 (6 H, 2 s, 2 OCH_3), 3.92 (1 H, s, CH), 6.32 (1 H, s, O–C=CH), 8.76 (1 H, br d, *J*=7.1 Hz, NH). ^{13}C NMR: δ 21.44 (C–*C*H_3), 24.29, 24.34, 25.23, 33.34 and 34.09 (5 CH_2), 42.06 (*C*–CH_3), 43.01 (*C*HCO_2CH_3), 50.33 (N–CH), 51.36 and 52.52 (2 OCH_3), 72.29 (O–C=*C*), 113.56 (O–C=*C*H), 157.41 (C), 169.27 and 172.15 (2 C=O, ester), 181.71 (C), 185.94 and 197.11 (2 C=O).

Diethyl 2-(cyclohexylamino)-4a-methyl-5,6-dioxo-4,4a,5,6-tetrahydrocyclopenta[*b*]pyran-3,4-dicarboxylate (7e)

Pale yellow crystals, mp 76–79 °C (from 2 : 1 hexane–ethyl acetate), 0.38 g, yield 95%. IR (KBr) (υ_{max}/cm^{-1}): 3240 (NH), 1765, 1713, 1664 (C=O). MS, *m*/*z* (%): 405 (M$^+$, 10), 332 (12), 281 (23), 232 (26), 105 (20), 80 (8), 73 (35), 41 (28), 28 (100). Anal. calcd for $C_{21}H_{27}NO_7$ (405.44): C, 62.21; H, 6.71; N, 3.45. Found: C, 62.2; H, 6.7; N, 3.5%. ^{1}H NMR: δ 1.13 and 1.29 (6 H, 2 t, *J*=7.1 Hz, 2 OCH_2C*H*$_3$), 1.36 (3 H, s, CH_3), 1.56–2.00 [10 H, m, C(CH_2)$_5$], 3.76 (1 H, m, NHC*H*), 3.98 (2 H, 2 dq, AMX_3 system, ^2J=10.8 Hz and ^3J=7.1 Hz, OC*H*$_2$$CH_3$), 4.00 (1 H, s, CH), 4.20 (2 H, 2 dq, AMX_3 system, ^2J=10.7 Hz and ^3J=7.1 Hz, OC*H*$_2$$CH_3$), 6.37 (1 H, s, O–C=CH), 8.86 (1 H, br d, *J*=7.7 Hz, NH). ^{13}C NMR: δ 13.90 and 14.43 (2 OCH_2C*H*$_3$), 21.56 (C–*C*H_3), 24.38, 24.42, 25.34, 33.41 and 34.18 (5 CH_2), 42.31 (*C*H$CO_2CH_2CH_3$), 43.10 (*C*–CH_3), 50.36 (N–CH), 60.04 and 61.54 (2 OCH_2CH_3), 72.70 (O–C=*C*), 113.57 (O–C=*C*H), 157.46 (C), 168.99 and 171.71 (2 C=O, ester), 181.96 (C), 186.03 and 197.43 (2 C=O).

Dimethyl 2-(2,6-dimethylanilino)-4a-methyl-5,6-dioxo-4,4a,5,6-tetrahydrocyclopenta[*b*]pyran-3,4-dicarboxylate (7f)

Yellow crystals, mp 178–180 °C (from 1 : 1 hexane–ethyl acetate), 0.36 g, yield 92%. IR (KBr) (υ_{max}/cm^{-1}): 3225 (NH), 1761, 1719 and 1666 (C=O). MS, *m*/*z* (%): 399 (M$^+$, 14), 340 (20), 312 (100), 280 (25), 224 (10), 105 (8), 80 (15), 59 (19). Anal. calcd for $C_{21}H_{21}NO_7$ (399.40): C, 63.15; H, 5.30; N, 3.51. Found: C, 63.2; H, 5.4; N, 3.5%. ^{1}H NMR: δ 1.45 (3 H, s, CH_3), 2.25 (6 H, s, 2 CH_3), 3.62 and 3.84 (6 H, 2 s, 2 OCH_3), 4.08 (1 H, s, CH), 6.22 (1 H, s, O–C=CH), 7.13 (2 H, d, *J*=7.2 Hz, 2 CH), 7.17 (1 H, t, *J*=7.2 Hz, CH), 10.08 (1 H, br s, NH). ^{13}C NMR: δ 18.47 (2 Ar–CH_3), 21.79 (C–*C*H_3), 42.18 (*C*HCO_2CH_3), 43.18 (*C*–CH_3), 51.84 and 52.79 (2 OCH_3), 74.03 (O–C=*C*), 114.19 (O–C=*C*H), 127.81 (CH, *para*), 128.43 (2 CH, *meta*), 133.27 and 135.87 (2 C, C_{ortho} and C_{ipso}), 157.07 (C), 169.45 and 172.03 (2 C=O, ester), 181.33 (C), 185.74 and 196.94 (2 C=O).

Diethyl 2-(2,6-dimethylanilino)-4a-methyl-5,6-dioxo-4,4a,5,6-tetrahydrocyclopenta[*b*]pyran-3,4-dicarboxylate (7g)

Yellow crystals, mp 120–123 °C (from 1 : 1 hexane–ethyl acetate), 0.38g, yield 90%. IR (KBr) (υ_{max}/cm^{-1}): 3240 (NH), 1760, 1713 and 1661 (C=O). MS, *m*/*z* (%): 427 (M$^+$, 12), 354 (5), 326 (100), 303 (23), 252 (31), 105 (26), 80 (14), 73 (15). Anal. calcd for $C_{23}H_{25}NO_7$ (427.45): C, 64.63; H, 5.90; N, 3.28. Found: C, 64.7; H, 5.9; N, 3.3%. ^{1}H NMR: δ 1.19 and 1.36 (6 H, 2 t, *J*=7.1 Hz, 2 CH_2C*H*$_3$), 1.46 (3 H, s, CH_3), 2.26 (6 H, s, 2 CH_3), 4.06 (2 H, m, ABX_3 system, OC*H*$_2$$CH_3$), 4.08 (1 H, s, CH), 4.28 (2 H, 2 dq, AMX_3 system, ^2J=10.8 Hz and ^3J=7.1 Hz, OC*H*$_2$$CH_3$), 6.21 (1 H, s, O–C=CH), 7.12 (2 H, d, *J*=7.2 Hz, 2 CH), 7.17 (1 H, t, *J*=7.2 Hz, CH), 10.10 (1 H, br s, NH). ^{13}C NMR: δ 14.21 and 14.38 (2 CH_2*C*H_3), 18.46 (2 Ar–CH_3), 21.86 (C–*C*H_3), 42.38 (*C*H$CO_2CH_2CH_3$), 43.20 (*C*–CH_3), 60.39 and 60.55 (2 O*C*H_2CH_3), 74.32 (O–C=*C*), 114.10 (O–C=*C*H), 127.74 (CH, *para*), 128.41 (2 CH, *meta*), 133.40 and 135.91 (2 C, C_{ortho} and C_{ipso}), 156.98 (C), 169.45 and 171.49 (2 C=O, ester), 181.60 (C), 185.82 and 197.19 (2 C=O).

Di-*tert*-butyl 2-(2,6-dimethylanilino)-4a-methyl-5,6-dioxo-4,4a,5,6-tetrahydrocyclopenta[*b*]pyran-3,4-dicarboxylate (7h)

Yellow crystals, mp 174–177 °C (from 1 : 1 hexane–ethyl acetate), 0.40 g, yield 85%. IR (KBr) (υ_{max}/cm^{-1}): 3230 (NH), 1761, 1712 and 1650 (C=O). MS, *m*/*z* (%): 483 (M$^+$, 10), 396 (7), 368 (16), 359 (20), 288 (12), 105 (10), 87 (32), 80 (26), 57 (100). Anal. calcd for $C_{27}H_{33}NO_7$ (483.56): C, 67.06; H, 6.88; N, 2.90. Found: C, 67.1; H, 6.8; N, 2.9%. ^{1}H NMR: δ 1.35 [9 H, s, $C(CH_3)_3$], 1.43 (3 H, s, CH_3), 1.56 [9 H, s, $C(CH_3)_3$], 2.26 (6 H, s, 2 CH_3), 3.89 (1 H, s, CH), 6.17 (1 H, s, O–C=CH), 7.12 (2 H, d, *J*=7.2 Hz, 2 CH), 7.16 (1 H, t, *J*=7.2 Hz, CH), 10.07 (1 H, br s, NH). ^{13}C NMR: δ 18.40 (2 Ar–CH_3), 21.97 (C–*C*H_3), 27.84 and 28.50 [2 C(*C*H_3)$_3$], 43.48 (*C*–CH_3), 43.79 [*C*H$CO_2C(CH_3)_3$], 76.07 (O–C=*C*), 80.97 and 82.46 [2 *C*(CH_3)$_3$], 113.75 (O–C=*C*H), 127.52 (CH, *para*), 128.31 (2 CH, *meta*), 133.74 and 135.96 (2 C, C_{ortho} and C_{ipso}), 156.66 (C), 168.80 and 170.46 (2 C=O, ester), 182.45 (C), 186.07 and 197.54 (2 C=O).

Acknowledgements

This research was supported by the National Research Council of the Islamic Republic of Iran (NRCI) as a National Research project under the grant number 989.

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