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Stereoselective synthesis of 1,2:4,5-di-*O*-isopropylidene-3-*C*-(5-phenyl-1,2,4-oxadiazol-3-yl)-β-D-psicopyranose and its X-ray crystallographic analysis

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Abstract

In a novel procedure, when 3-*O*-benzoyl-3-*C*-(*N*-hydroxycarbamimidoyl)-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose (**1**) is treated with acetic anhydride, chloroacetyl chloride, propanic anhydride and benzoyl chloride, the 3-*O*-benzoyl group undergoes an intramolecular replacement reaction with neighbouring group participation and transfer resulting in a more stable conjugated system by the formation of a 1,2,4-oxadiazol ring. A possible mechanism is reported. The structure has been determined by spectroscopic data and X-ray crystallographic analysis.

1. Introduction

The methodologies of branched-chain sugar synthesis have attracted considerable attention[1] because of their biological importance. Recently, a number of oxadiazolines have been reported to possess anti-HIV activity.[2] These findings prompted us to synthesise oxadiazole moieties and incorporate them with carbohydrate fragments.[3] Here, we would like to report a novel procedure in which the 3-*O*-benzoyl group undergoes an intramolecular replacement reaction with neighbouring group participation and transfer in the formation of a 1,2,4-oxadiazol ring when 3-*O*-benzoyl-3-*C*-(*N*-hydroxycarbamimidoyl)-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose (**1**) is treated with acetic anhydride, chloroacetyl chloride, propanic anhydride or benzoyl chloride. A possible mechanism for its formation, as well as its structural analysis, is described.

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2. Results and discussion

For our purpose, we chose the most frequently encountered route for the synthesis of substituted 1,2,4-oxadiazoles involving the acylation and subsequent cyclization of amidoximes.[4–6] Thus, the key intermediate would be of 1,2:4,5-di-*O*-isopropylidene-3-*C*-amidoximino-3-*O*-benzoyl-β-D-psicopyranose (**1**), which was obtained in the yield of 48%, by controlling the pH of the reaction mixture between pH 7 and 8, through refluxing of 3-*O*-benzoyl-3-*C*-cyano-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose with hydroxylamine in anhydrous methanol.[7] The amidoxime **1** was then treated with different acylation agents for ring closure giving the substituted 1,2,4-oxadiazole derivatives. First of all, it was treated with acetic anhydride at 80 °C under nitrogen atmosphere for 18 h, presumably giving 1,2:4,5-di-*O*-isopropylidene-3-*C*-(5-methyl-1,2,4-oxadiazol-3-yl)-3-*O*-benzoyl-β-D-psicopyranose (**2**). The FABMS and ESIMS all gave m/z 427 $[M+Na]^+$, 443 $[M+K]^+$ and 405 $[M+1]^+$ which indicated its molecular formula to be $C_{20}H_{24}N_2O_7$ (**3**) and not $C_{22}H_{26}N_2O_8$ which is the substituted 1,2,4-oxadiazole derivative **2** we desired. The characteristics from the H–H COSY, DEPT and

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TOCSY spectra by comparison with 3-*C*-cyano-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose, 3-*O*-acetyl-3-*C*-cyano-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose, 3-*O*-benzoyl-3-*C*-cyano-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose, 3-*O*-benzoyl-3-*C*-cyano-1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose and 3-*O*-benzoyl-3-*C*-(*N*-hydroxycarbamimidoyl)-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose (**1**)[7] showed that the 1,2:4,5-di-*O*-isopropylidene-D-pyranose fragment still remained in **3**. Thus the remainder is $C_8H_6N_2O_2$, in which two parts of it contained as 5-phenyl-1,2,4-oxadiazol-3-yl [$C_8H_5N_2O$] on the basis of NMR spectral data with a hydroxyl group –OH at ν_{max}: 3397.0 (s, OH) cm^{-1}, δ_H: 3.33 (1H, s, HO-3, exchangeable with D_2O).[4–6] We tried to determine the configuration of C-3 by a NOESY spectrum, but the problem was that there were no correlations between HO-3 or benzene hydrogens and H-2, 4, 5 and 6 of sugar ring. We fortunately obtained the crystals of **3** from 1:1 acetone–cyclohexane that were suitable for X-ray crystallographic analysis.

Table 1
Crystal data and structure refinement for **3**

Empirical formula	$C_{20}H_{24}N_2O_7$
Formula weight	404.41
Temperature	291(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	$a = 10.309(1)$ Å, $\alpha = 90°$ $b = 10.474(1)$ Å, $\beta = 90°$ $c = 18.646(3)$ Å, $\gamma = 90°$
Volume, Z	2013.3(4) $Å^3$, 4
$D_{calc.}$	1.334 Mg/m^3
Absorption coefficient	0.102 mm^{-1}
$F(000)$	856
Crystal size	$0.56 \times 0.50 \times 0.42$ mm
θ Range for data collection	2.18 to 26.99°
Limiting indices	$0 \le h \le 13$, $0 \le k \le 13$, $1 \le l \le 23$
Reflections collected	2766
Independent reflections	2625 ($R_{int} = 0.0180$)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2625/0/268
Goodness-of-fit on F^2	0.914
Final R indices [$I > 2\sigma(I)$]	$R^1 = 0.0334$, $WR^2 = 0.0662$
R indices	$R^1 = 0.0526$, $WR^2 = 0.0711$
Absolute structure parameter	2.0 (11)
Extinction coefficient	0.0283 (13)
Largest diff. peak and hole	0.147 and 0.137 e $Å^{-3}$

Table 2
Fractional atomic coordinates ($\times 10^4$) and equivalent thermal parameters of **3**

Atom	x	y	z	$U(eq) \times 10$
O-1	1189(2)	2036(1)	287(1)	52(1)
O-2	2332(1)	1450(1)	1262(1)	43(1)
O-3	4526(1)	4018(1)	802(1)	43(1)
O-4	5169(1)	3804(1)	2248(1)	50(1)
O-5	6471(1)	2452(2)	1620(1)	52(1)
O-6	4311(2)	1385(1)	638(1)	46(1)
O-7	1023(2)	5103(2)	1974(1)	61(1)
N-1	2061(2)	4232(2)	2059(1)	59(1)
N-2	1986(2)	4946(2)	926(1)	40(1)
C-1	2480(2)	2403(2)	136(1)	47(1)
C-2	3212(2)	2123(2)	828(1)	39(1)
C-3	3693(2)	3302(2)	1253(1)	35(1)
C-4	4373(2)	2835(2)	1943(1)	39(1)
C-5	5328(2)	1758(2)	1809(1)	46(1)
C-6	4974(2)	830(2)	1233(1)	52(1)
C-7	1234(2)	1083(2)	828(1)	45(1)
C-8	1461(2)	218(2)	503(1)	58(1)
C-9	34(2)	1181(3)	1273(2)	68(1)
C-10	2573(2)	4178(2)	1426(1)	38(1)
C-11	1059(2)	5475(2)	1287(1)	40(1)
C-12	85(2)	6396(2)	1037(1)	41(1)
C-13	650(2)	7115(2)	1509(1)	49(1)
C-14	1539(2)	7985(2)	1253(1)	57(1)
C-15	1693(2)	8144(2)	528(2)	60(1)
C-16	974(2)	7432(3)	55(1)	60(1)
C-17	89(2)	6553(2)	308(1)	51(1)
C-18	6508(2)	3502(2)	2099(1)	57(1)
C-19	7175(3)	3129(3)	2789(2)	91(1)
C-20	7151(3)	4612(3)	1739(2)	88(1)

Crystallographic data, and details on data collection and structure refinement are summarized in Table 1. The coordinates of the non-hydrogen atoms are listed in Table 2. The bond lengths and bond angles are listed in Tables 3 and 4, respectively. The ORTEP plot for compound **3** is shown in Fig. 1 together with the numbering scheme, and the packing arrangement of the molecules is shown in Fig. 2. The pyranoid ring retains a $_4C^1$ chair conformation, 5-phenyl-1,2,4-oxadiazole and 3-OH groups are bonded to C-3 in equatorial and axial positions, respectively. The X-ray diffraction analysis also indicates that the crystal has molecular stacking along a one-dimensional chain. Fig. 2 exhibits the interaction among the molecules in the columnar stacking. The molecules assemble through 3-OH···O-1 intermolecular hydrogen bonds (2.88 Å; 157.1°).

In order to confirm the unexpected reaction and study the mechanism more deeply, we explored the reactions of **1** with chloroacetyl chloride, propanoic anhydride or benzoyl chloride instead of acetic anhydride, at 120–130 °C under nitrogen atmosphere for 22 h. Only one product, the 5-phenyloxadiazole **3**, but not

4–**6**, was obtained in yields 81–88% from each of the above three reactions. The products were homogeneous as evidenced by TLC and had the same sharp melting point as well as correct elemental analyses, IR, MS and ^{1}H, and ^{13}C NMR spectral data (Scheme 1).

Table 3
The bond lengths (Å) for **3**

O(1)–C(1)	1.414(3)	C(2)–C(3)	1.549(3)
O(1)–C(7)	1.420(2)	C(3)–C(10)	1.510(3)
O(2)–C(2)	1.405(2)	C(3)–C(4)	1.544(3)
O(2)–C(7)	1.443(2)	C(4)–C(5)	1.518(3)
O(3)–C(3)	1.417(2)	C(5)–C(6)	1.493(3)
O(4)–C(4)	1.424(2)	C(11)–C(12)	1.468(3)
O(4)–C(18)	1.444(3)	C(12)–C(17)	1.381(3)
O(5)–C(18)	1.417(3)	C(12)–C(13)	1.385(3)
O(5)–C(5)	1.430(3)	C(13)–C(14)	1.378(3)
O(6)–C(2)	1.416(2)	C(14)–C(15)	1.372(3)
O(6)–C(6)	1.427(3)	C(15)–C(16)	1.372(3)
O(7)–C(11)	1.339(2)	C(16)–C(17)	1.379(3)
O(7)–N(1)	1.415(2)	C(7)–C(9)	1.492(3)
N(1)–C(10)	1.293(3)	C(7)–C(8)	1.510(3)
N(2)–C(11)	1.293(3)	C(18)–C(20)	1.497(4)
N(2)–C(10)	1.372(3)	C(18)–C(19)	1.511(4)
C(1)–C(2)	1.525(3)		

Table 4
The bond angles (°) for **3**

C(2)–O(6)–C(6)	114.21(16)	O(1)–C(1)–C(2)	104.15(18)
C(1)–O(1)–C(7)	107.59(16)	O(2)–C(2)–O(6)	112.79(16)
C(2)–O(2)–C(7)	108.57(15)	O(2)–C(2)–C(1)	105.30(16)
C(4)–O(4)–C(18)	108.53(16)	O(6)–C(2)–C(1)	106.76(17)
C(18)–O(5)–C(5)	105.15(17)	O(2)–C(2)–C(3)	108.22(16)
C(11)–O(7)–N(1)	105.81(16)	O(6)–C(2)–C(3)	107.91(15)
C(10)–N(1)–O(7)	103.64(17)	C(1)–C(2)–C(3)	116.00(17)
C(11)–N(2)–C(10)	102.94(17)	O(3)–C(3)–C(10)	105.60(15)
O(3)–C(3)–C(4)	112.80(16)	N(1)–C(10)–C(3)	122.26(19)
C(10)–C(3)–C(4)	111.21(16)	N(2)–C(10)–C(3)	123.29(18)
O(3)–C(3)–C(2)	108.18(15)	N(2)–C(11)–O(7)	113.19(19)
C(10)–C(3)–C(2)	110.40(16)	N(2)–C(11)–C(12)	128.40(2)
C(4)–C(3)–C(2)	108.58(15)	O(7)–C(11)–C(12)	118.42(19)
O(4)–C(4)–C(5)	102.82(16)	C(17)–C(12)–C(13)	119.40(2)
O(4)–C(4)–C(3)	111.63(16)	C(17)–C(12)–C(11)	118.70(2)
C(5)–C(4)–C(3)	113.11(17)	C(13)–C(12)–C(11)	121.90(2)
O(5)–C(5)–C(6)	110.81(19)	C(14)–C(13)–C(12)	120.20(2)
O(5)–C(5)–C(4)	101.38(16)	C(15)–C(14)–C(13)	120.00(2)
C(6)–C(5)–C(4)	116.31(18)	C(14)–C(15)–C(16)	120.30(2)
O(6)–C(6)–C(5)	114.31(18)	C(15)–C(16)–C(17)	120.10(2)
N(1)–C(10)–N(2)	114.42(19)	C(16)–C(17)–C(12)	120.10(2)
O(1)–C(7)–O(2)	103.69(16)	O(5)–C(18)–O(4)	105.43(17)
O(1)–C(7)–C(9)	108.60(2)	O(5)–C(18)–C(20)	109.40(2)
O(2)–C(7)–C(9)	108.70(17)	O(4)–C(18)–C(20)	109.90(2)
O(1)–C(7)–C(8)	110.73(18)	O(5)–C(18)–C(19)	110.40(2)
O(2)–C(7)–C(8)	110.13(19)	O(4)–C(18)–C(19)	109.10(2)
C(9)–C(7)–C(8)	114.40(2)	C(20)–C(18)–C(19)	112.40(2)

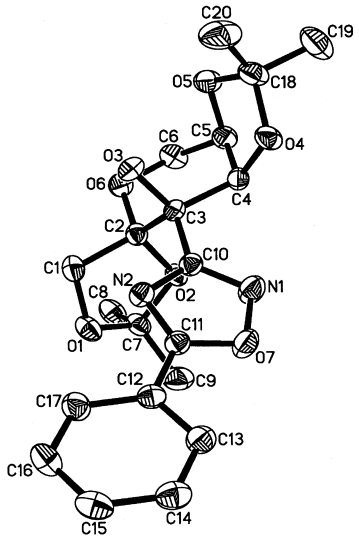


Fig. 1. The ORTEP plot for compound **3**.

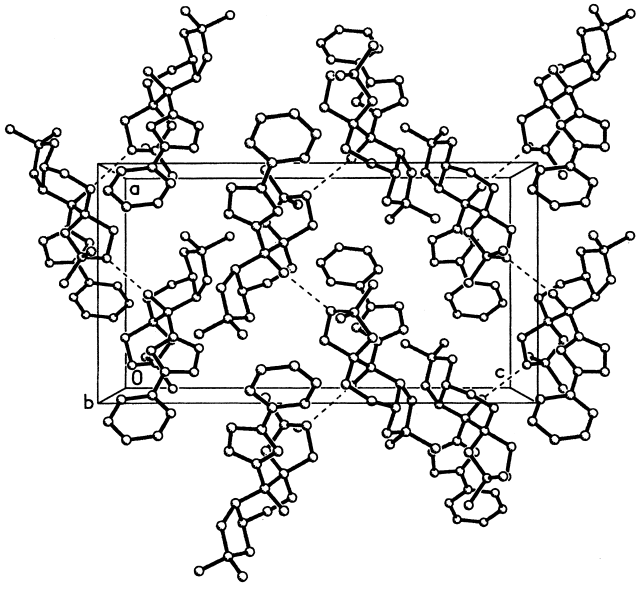


Fig. 2. The arrangement of the molecules in the unit cell.

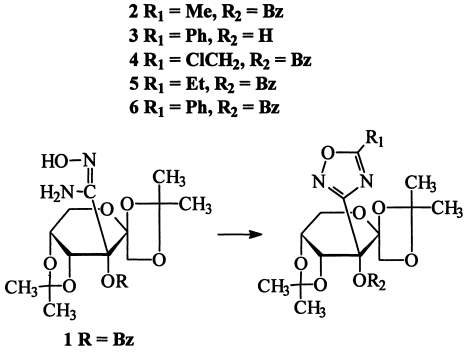
Taking these facts into account, we believe that the 3-*O*-benzoyl group undergoes intramolecular replacement reaction through neighbouring group participation, and a more stable conjugation system is formed in compound **3** during the cyclization of **1** with acetic anhydride, $ClCH_2COCl$, propanic anhydride or benzoyl chloride. As shown in Scheme 2, the novel procedure proceeds as follows: acetylation of amidoxime **1** takes place first at the hydroxyl group to form 3-*C*-(*N*-acetoxycarbamimidoyl)-3-*O*-benzoyl-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose (**A**).[6] The lone electron pair on NH_2 with high density attacks the carbon of the C=O group in the 3-*O*-benzoyl group to produce the intramolecular replacement reaction through neigh-

bouring-group participation and transfer. The resulting intermediate **B** undergoes ring-closure reactions with the action of anhydrides or benzoyl chloride under refluxing to remove the hydrogen from NH_2 and give rise to the compound **3**.

3. Experimental

3.1. General procedures

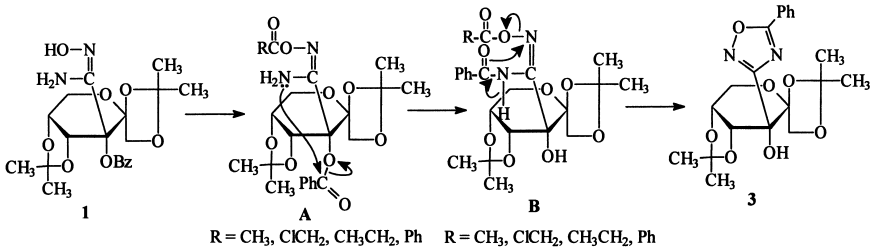
Melting points were determined using an X_4 micromelting point apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 241MC polarimeter. IR spectra were recorded with a Biorad FT-40 spectrophotometer (KBr pellets). All NMR spectra were recorded on a Varian MERCURY 400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C) with $CDCl_3$ as solvent, Me_4Si as an internal standard. Mass spectra were obtained on either ZAB-HS or HP 1100-MSD mass spectrometers. Column chromatography was performed on silica gel (200–300 mesh), and silica gel GF_{254} for TLC was purchased from the Qingdao Chemical Company (China). Detection was effected by spraying the plates with 5% ethanolic H_2SO_4 (followed by heating at 110 °C for 10 min) or by direct UV irradiation of the plate. All the crystallographic measurements were carried out on a KUMA KM-4 diffractometer with graphite-monochromated MoKα radiation in a θ/2θ scan mode. The unit cell parameters were determined from least-squares refinement based on the setting angles of 25 reflections. The stability of conditions was controlled by three control measurements every hundred reflections.



Scheme 1. Reaction conditions: Ac_2O, $ClCH_2COCl$, $(CH_3CH_2CO)_2O$ or benzoyl chloride, respectively, N_2, 80 or 120–130 °C.

3.1.1. 3-*O*-Benzoyl-3-*C*-(*N*-hydroxycarbamimidoyl)-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose (1). A solution of 3-*O*-benzoyl-3-*C*-cyano-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose (1.20 g, 3.08 mmol) and hydroxylamine (6.5 mmol) in anhyd MeOH (15 mL) (pH 7–8) was refluxed with stirring for 8 h. After the reaction was complete (TLC 1:2 cyclohexane–EtOAc), the solvent was removed by distillation, the residue was purified by silica gel column chromatography with 2:3 cyclohexane–EtOAc to afford **1** (0.75 g, 58%) as white crystals: mp 109–112 °C, R_f 0.62 (1:2 cyclohexane–EtOAc), $[\alpha]_D^{22}$ −102.3° (*c* 1.0, CH_2Cl_2). ν_{max}: 3394.0 (vs, OH, NH_2), 1687.0 (m, CO) cm^{-1}; δ_H: 9.85 (1H, bs, OH, exchangeable with D_2O), 8.11–7.45 (5H, m, Ph–H), 5.23 (2H, s, NH_2, exchangeable with D_2O), 4.81 (1H, d, $J_{1,1'}$ 7.5 Hz, H-1), 3.82 (1H, d, H-1′), 5.61 (1H, d, $J_{4,5}$ 7.8 Hz, H-4), 4.43 (1H, ddd, $J_{5,6}$ 2.7 Hz, $J_{5,6'}$ 6.0 Hz, H-5), 4.18 (1H, dd, $J_{6,6'}$ 10.8 Hz, H-6), 3.86 (1H, dd, H-6′), 1.55, 1.53, 1.50, 1.41 (12H, 4s, 4 × CH_3) ppm; δ_C: 170.71 (C=O), 151.86 (C=N), 133.59, 130.19, 128.42 (Ph–C), 111.86, 103.30 (2 × CMe_2), 73.92 (C-1), 110.97 (C-2), 73.45 (C-3), 75.73 (C-4), 65.04 (C-5), 63.04 (C-6), 26.63, 26.19, 25.96, 25.01 (4 × CH_3) ppm; ESIMS (%): *m*/*z* 445 $[M + Na]^+$(100). Anal. Calcd for $C_{20}H_{26}N_2O_8$: C, 56.80; H, 6.16; N, 6.64. Found: C, 56.76; H, 6.18; N, 6.70.

3.1.2. 1,2:4,5-Di-*O*-isopropylidene-3-*C*-(5-phenyl-1,2,4-oxadiazol-3-yl)-β-D-psicopyranose (3). A solution of **1** (0.20 g, 0.47 mmol) in redistilled Ac_2O (8 mL) was heated at 80 °C under a nitrogen atmosphere for 18 h until TLC (1:2 acetone–cyclohexane) showed the reaction complete. Anhyd EtOH (10 mL) was added with stirring for 30 min. Then the solvent was distilled off, and the residue was further coevaporated with toluene. The resultant brown syrup was purified on a column of silica gel using 1:3 acetone–cyclohexane as eluent to give white crystals **3** (0.17 g, 88%): mp 116–117 °C, R_f 0.26 (1:2 acetone–cyclohexane), $[\alpha]_D^{22}$ −148.5° (*c* 1.0,



Scheme 2. A possible mechanism for the intramolecular replacement reaction to form **3**.

CH_2Cl_2). ν_{max}: 3397.0 (s, OH), 1603.0 (s, C=N), 1555.0 (s, C–N) cm^{-1}; δ_H: 8.16 (2H, dd, $J_{2,3} = J_{5,6} = 6.0$ Hz, $J_{2,4} = J_{4,6} = 1.8$ Hz, ArH-2,6), 7.57 (1H, dd, $J_{3,4} = J_{4,5} = 4.8$ Hz, ArH-4), 4.60 (1H, d, $J_{1,1'}$ 9.5 Hz, H-1), 4.03 (1H, d, H-1′), 5.23 (1H, d, $J_{4,5}$ 5.5 Hz, H-4), 4.41 (1H, m, H-5), 4.37 (1H, dd, $J_{5,6}$ 3.0 Hz, $J_{6,6'}$ 12.5 Hz, H-6), 4.30 (1H, dd, H-6′), 3.33 (1H, s, HO-3), 1.63, 1.48, 1.43, 1.11 (12H, 4s, $4 \times CH_3$) ppm; δ_C: 175.84 (C-3′), 170.89 (C-5′), 132.83, 129.05, 128.23, 124.01 (Ph–C), 112.97, 105.36 ($2 \times CMe_2$), 72.18 (C-1), 109.58 (C-2), 71.89 (C-3), 73.83 (C-4), 71.01 (C-5), 60.03 (C-6), 25.04, 25.79, 25.64, 25.21 ($4 \times CH_3$) ppm; FABMS (%): m/z 405 $[M + 1]^+$(100). Anal. Calcd for $C_{20}H_{24}N_2O_7$: C, 59.40; H, 5.94; N, 6.93. Found: C, 59.38; H, 5.96; N, 6.91.

Compound **1** (0.20 g, 0.47 mmol) was heated with $ClCH_2COCl$, propanoic anhydride and benzoyl chloride (10 mL), respectively, at 120–130 °C under nitrogen atmosphere for 22 h until TLC (1:2 acetone–cyclohexane) showed the reaction complete. The mixture was then poured into ice-water, extracted with CH_2Cl_2 (3×20 mL), washed, dried (Na_2SO_4), concentrated and purified by column chromatography on silica gel to give compound **3** (81–83%) as white crystals, which was consistent with the product obtained in the above procedure in all physical and spectral data.

4. Supplementary material

Full crystallographic details, excluding structure features, have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel. +44 1223 336408; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk; web: http://www.ccdc.cam.uk/conts/retrieving/html.

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