Synthesis and X-ray diffraction data of 5-acryloyloxy-*trans*-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzo[*b*]furan

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The compound O-acryloylated 2,3-dihydrobenzo[b]furan-5-ol (**2**) described in the title (chemical formula $C_{19}H_{18}O_4$) was synthesized through the acryloylation reaction in anhydrous dichloromethane from the corresponding *trans*-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzo[b]furan-5-ol derivative (**1**), an adduct easily obtained using the Lewis acid-promoted formal [3 + 2] cycloaddition reaction. Molecular characterization was performed by Fourier Transform-Infrared (FT-IR), Gas Chromatography-Mass Spectrometry (GC-MS), ^{1}H and ^{13}C NMR and crystallographic characterization was carried out by X-ray diffraction (XRD) of polycrystalline samples. The title compound crystallized in a monoclinic system and unit-cell parameters are reported [$a = 8.067(2)$ Å, $b = 8.803(2)$ Å, $c = 22.405(5)$ Å, $\beta = 91.62(3)°$, unit-cell volume $V = 1590.7(6)$ Å^3 and $Z = 4$]. All measured lines were indexed with the $P2_1/c$ (No. 14) space group. © *2012 International Centre for Diffraction Data.*
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Key words: dihydrobenzofuran, X-ray powder diffraction data, *O*-acryloylation reaction

I. INTRODUCTION

Benzofuran and dihydrobenzofuran derivatives are natural and synthetic medicinally important heterocyclic molecules (Benavides *et al.*, 1999; Apers *et al.*, 2003). The chemistry of these compounds has been very interesting for organic chemists, owing to the presence of scaffolds on the skeletons of numerous natural products and pharmaceutical agents (Tsai *et al.*, 1998; Chen *et al.*, 2002). A large number of reports have shown that these compounds exhibit a broad spectrum with potential bioactivities, such as antiplasmodial (Rakotondramanana *et al.*, 2007), antileishmanial (Van Miert *et al.*, 2005), antimicrobial (Kossakowski *et al.*, 2009) and anti-inflammatory (Wu *et al.*, 2011). In general, many synthetic methods for the synthesis of (dihydro)benzofuran systems have been developed (Bertolini and Pineschi, 2009). Among them, the Lewis acid-promoted formal [3 + 2] cycloaddition reaction is a powerful and successful synthetic tool to rapidly construct this ring system (Engler *et al.*, 1994, 1996; Engler and Lyenyar, 1998). Interesting chemical transformation with propenylbenzenes is this cycloaddition catalyzed by $Fe(ClO_4)_3$ (Ohara *et al.*, 2002, 2003), $InCl_3$ (Yadav *et al.*, 2003) for obtaining the *trans*-2,3-dihydrobenzo[*b*]furan-5-ols derivatives have been reported. We have also described the diastereoselective synthesis of corresponding *trans*-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzo[b]furan-5-ol (**1**) using BF_3OEt_2 as catalyst and PEG-400 as a green and reusable solvent (Kouznetsov *et al.*, 2008). However, few crystallographic studies by X-ray diffraction (XRD) of this type of derivative have been reported.

In this regard, our ongoing research program focused on the bioactive dihydrobenzofuran derivatives with anethole fragments and its X-ray crystallographic study. Here, we discuss a simple methodology for preparation of compound 5-acryloyloxy-*trans*-2-(4-methoxiphenyl)-3-methyl-2,3-dihydrobenzo[*b*]furan (**2**) through the acryloylation reaction starting from the corresponding 2,3-dihydrobenzo[*b*]furan-5-ol (**1**) and report the results of the molecular characterization (FT-IR, GC-MS, ^{1}H-NMR and ^{13}C-NMR) and X-ray powder diffraction (XRPD) data.

II. EXPERIMENTAL

A. Synthesis

As shown in Figure 1, the title compound was synthesized as follows: a mixture of *trans*-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzo[*b*]furan-5-ol (**1**) (0.50 g, 1.95 mmol) and triethylamine (0.39 g, 3.91 mmol) in CH_2Cl_2 (30 ml) was stirred at room temperature, after 10 min the system was cooled to 0 °C and a solution of acryloyl chloride (0.35 g, 3.91 mmol) was added dropwise via syringe for 5 min into the mixture. The resulting mixture was stirred vigorously at room temperature overnight (about 14–16 h). After completion of the reaction as indicated by Thin Layer Chromatography (TLC), the final reaction mixture was placed at 0 °C and was carefully diluted with water (20 ml) and extracted with dichloromethane (3 × 15 ml). The organic layer was separated and dried (Na_2SO_4), concentrated *in vacuo* and the crude product was purified by column chromatography using silica gel (60–120 mesh) and eluted with petroleum ether – ethyl acetate to afford pure dihydrobenzofuran (**2**) (yield 82%). The melting point was between 99 and 101 °C.

The molecular characterization that was carried out with infrared (IR) spectrometry showed the following characteristic signals: 3007, 2953, 2884, 1734, 1610 and 1515 cm^{-1}; Mass Spectrometry (MS) gave a molecular peak $m/z = 310$ (60, M^+);

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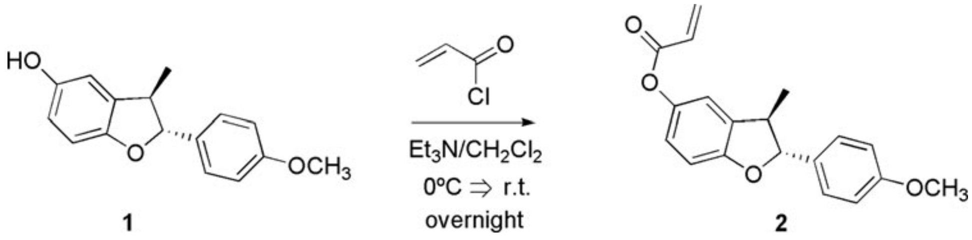

Figure 1. Synthesis of the 5-acryloyloxy-*trans*-2-(4-methoxiphenyl)-3-methyl-2,3-dihydrobenzo[*b*]furan (**2**) via acryloylation reaction.

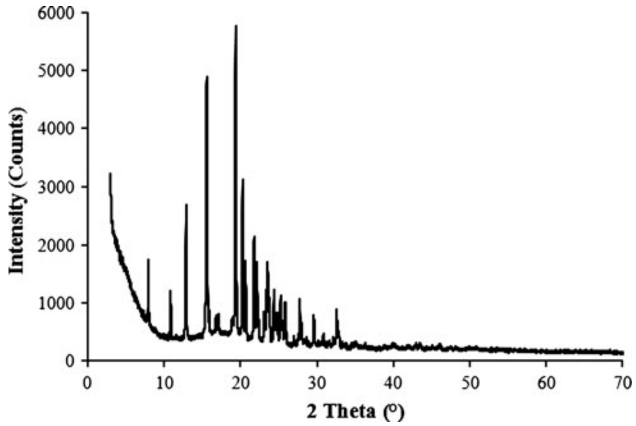

Figure 2. XRPD pattern of 5-acryloyloxy-*trans*-2-(4-methoxiphenyl)-3-methyl-2,3-dihydrobenzo[*b*]furan (**2**).

nuclear magnetic resonance on protons ^{1}H NMR (400 MHz, $CDCl_3$ Me_4Si) showed δ (ppm) to be 1.39 (3H, d, $J = 6.8$ Hz, $-CH_3$), 3.47 (1H, m, 3-H), 3.82 (3H, s, CH_3O-Ar), 5.15 (1H, d, $J = 9.3$ Hz, 2-H), 6.00 (1H, dd, $J = 9.3$, 1.1 Hz, H_{vinyl}), 6.33 (1H, dd, $J = 17.3$, 10.4 Hz, H_{vinyl}), 6.61 (1H, dd, $J = 17.3$, 1.1 Hz, H_{vinyl}), 6.83 (1H, d, $J = 8.3$ Hz, 6-H), 6.92 (4H, m, 4-H, 7-H y 2-H_{Ar}) and 7.37 (2H, d, $J = 8.6$ Hz, 3-H_{Ar}); nuclear magnetic resonance on carbons ^{13}C-NMR (100 Hz, $CDCl_3$ Me_4Si), δ (ppm), presents the following data: 165.1, 159.7, 156.8, 144.4, 133.1, 132.2, 132.2, 128.0, 127.6 (2C), 120.9, 117.0, 114.0 (2C), 109.5, 93.0, 55.2, 45.4, and 17.4.

B. Powder data collection

The title compound was ground and sieved to grain size less than 38 μm. The compound was mounted on a zero-

TABLE I. XRPD data of 5-acryloyloxy-*trans*-2-(4-methoxiphenyl)-3-methyl-2,3-dihydrobenzo[b]furan (**2**).

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_0)_{obs}$	h	k	l	$2\theta_{calc}$ (°)	d_{calc} (Å)	$\Delta 2\theta$ (°)
7.877	11.2149	13	0	0	2	7.889	11.1984	0.012
10.773	8.2057	10	0	1	1	10.789	8.1936	0.016
12.794	6.9137	32	0	1	2	12.780	6.9211	−0.014
15.482	5.7188	76	1	1	1	15.485	5.7179	0.003
15.801	5.6041	6	0	0	4	15.815	5.5992	0.014
16.723	5.2971	6	−1	1	2	16.720	5.2982	−0.003
17.014	5.2072	6	1	1	2	17.014	5.2071	0.00
18.822	4.7109	5	−1	1	3	18.868	4.6996	0.046
19.268	4.6028	100	1	1	3	19.260	4.6046	−0.008
20.156	4.4020	38	0	2	0	20.156	4.4019	0.00
20.544	4.3197	20	0	2	1	20.546	4.3193	0.002
21.671	4.0976	27	0	2	2	21.675	4.0968	0.004
			1	1	4	22.013	4.0346	
22.033	4.0310	19	2	0	0	22.027	4.0322	−0.006
22.254	3.9915	5	0	1	5	22.249	3.9923	−0.005
22.997	3.8642	7	−1	2	0	2.999	3.8638	0.002
23.415	3.7962	20	1	2	1	23.398	3.7989	−0.017
			0	2	3	23.442	3.7919	
23.628	3.7624	11	2	0	2	23.644	3.7599	0.016
			−1	2	2	24.246	3.6679	
24.253	3.6669	13	2	1	0	24.259	3.6660	0.006
			1	2	2	24.453	3.6373	
24.494	3.6313	5	−2	1	1	24.484	3.6328	−0.010
25.127	3.5413	12	1	1	5	25.119	3.5424	−0.008
25.723	3.4592	12	0	2	4	25.723	3.4606	−0.010
			2	1	2	25.744	3.4577	
27.338	3.2597	2	2	1	3	27.356	3.2575	0.018
27.608	3.2284	12	2	0	4	27.604	3.2288	−0.004
27.870	3.1986	6	−1	2	4	27.853	3.2005	−0.017
28.219	3.1599	2	1	2	4	28.217	3.1601	−0.002

Continued

TABLE I. Continued

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_0)_{obs}$	h	k	l	$2\theta_{calc}$ (°)	d_{calc} (Å)	$\Delta 2\theta$ (°)
			0	2	5	28.405	3.1397	
28.440	3.1358	2	1	1	6	28.474	3.1321	0.034
29.450	3.0305	8	2	1	4	29.441	3.0314	−0.009
30.032	2.9731	1	2	2	0	30.030	2.9733	−0.002
			−1	2	5	30.319	2.9456	
30.362	2.9415	1	2	2	1	30.384	2.9394	0.022
30.714	2.9086	3	0	3	1	30.702	2.9098	−0.012
			1	2	5	30.740	2.9063	
			−1	1	7	31.446	2.8425	
31.516	2.8364	<1	0	3	2	31.489	2.8388	−0.027
32.011	2.7937	3	1	1	7	32.016	2.7933	0.005
32.441	2.7576	10	1	3	0	32.440	2.7577	−0.001
			2	2	3	32.623	2.7426	
2.7387	32.671	4	−1	3	1	32.652	2.7403	−0.019
			−1	2	6	33.115	2.7030	
2.7002	33.151	<1	2	0	6	33.137	2.7012	−0.014
			−1	0	8	33.558	2.6683	
			0	1	8	33.563	2.6679	
2.6650	33.602	1	1	2	6	33.581	2.6665	−0.021
2.5983	34.491	1	0	3	4	34.477	2.5993	−0.014
			3	0	2	34.506	2.5972	
			−1	3	3	34.535	2.5951	
2.5698	34.885	2	3	1	0	34.869	2.5709	−0.016
2.5527	35.126	<1	−1	1	8	35.113	2.5536	−0.013
2.4843	36.126	<1	−1	3	4	36.138	2.4835	0.012
			−1	2	7	36.177	2.4809	
2.3312	38.589	<1	−2	0	8	38.596	2.3309	0.007
			−2	3	2	38.626	2.3291	
			−2	1	8	39.981	2.2532	
2.2521	40.002	1	1	2	8	39.994	2.2525	−0.008
			2	3	3	40.033	2.2505	
2.1664	41.656	1	0	2	9	41.658	2.1663	−0.002
			−2	3	5	42.794	2.1114	
			0	4	3	42.800	2.1111	
2.1091	42.844	1	−1	1	10	42.812	2.1106	−0.032
2.0900	43.254	2	3	1	6	43.233	2.0910	−0.021
			−1	4	2	43.276	2.0890	
			1	4	4	1.9804	45.779	
1.9787	45.821	2	−3	3	1	1.9781	45.835	0.014
			3	1	7	1.9780	45.837	

background specimen holder. The diffraction pattern was collected at room temperature (298 K) in the 2θ range from 2 to 70° 2θ with a step size of 0.02° 2θ and a count time of 0.4 s per step, using a D8 FOCUS BRUKER diffractometer operating in Bragg–Brentano geometry quipped with an X-ray tube (Cu$K\alpha$ radiation: $\lambda = 1.5406$ Å, 40 kV and 40 mA) with a nickel filter and a one-dimensional LynxEye detector. A fixed anti-scatter slit of 8 mm, receiving slit of 1 mm, soller slits of 2.5° and a detector slit of 3 mm were used.

Table II. Crystal-structure data for 5-acryloyloxy-*trans*-2-(4-methoxiphenyl)-3-methyl-2,3-dihydrobenzo[*b*]furan (**2**).

Crystal system	Monoclinic
a (Å)	8.0676 (7)
b (Å)	8.803 (2)
c (Å)	22.4057 (2)
B (º)	91.627 (3)
V (Å^3)	1590.7 (2)
Z	4
M_{20}	22.9
F_{30}	42.9 (0.0108, 65)
D_m	1.447 g cm^{-3}

PowderX program (Dong, 1999) was used to remove the background (Sonneveld and Visser, 1975), smoothing (Savitzky and Golay, 1964), to eliminate the $K\alpha_2$ component (Rachinger, 1948) and the second derivative method was used to determine the peak observed positions and intensities.

III. RESULTS AND DISCUSSION

The experimental XRPD pattern is depicted in Figure 2. XRPD data for the title compound are given in Table I. Indexing of the experimental XRPD pattern was done using the DICVOL06 program (Boultif and Louër, 2006) with an absolute error of 0.03° 2θ. The title compound crystallized in a monoclinic system with space group $P2_1/c$ (No. 14) estimated by the CHEKCELL program (Laugier and Bochu, 2002), which was compatible with the systematic absence and with the crystal density (1.447 g cm^{-3}). The unit-cell parameters were refined with the NBS*AIDS83 program (Mighell *et al.*, 1981). Unit-cell data, values of M_{20} (de Wolff, 1968) and F_{30} (Smith and Snyder, 1979) are presented in Table II.

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