Biosci. Biotech. Res. Comm. Special Issue No 1:130-132 (2017)

BBRC
Bioscience Biotechnology Research Communications

Synthesis and some properties of 3-substituted-5,5-Dimethyl-5,6-dihydrobenzo[H]quinazolin(1h,3h)2,4-dione

Najmeh Torshirzad

Department of Food Science and Technology, Torbat-e Heydarieh Branch, Islamic Azad University Torbat-e Heydarieh, Iran

ABSTRACT

Ethyl 2-cyano-3,3-dimethyl-4-phenylbutanoate was cyclized into 1-amino-3,3-dimethyl-3,4-dihydronaphthalene-2-ethylcarboxyiate condensation of which with primary amines synthesized 3 – substituted-5,5-dimethyl-5,6-dihydrobenzo[h]quinazolin-(1H,3H)2,4-dions. The method is based on the interaction of carbamate (II) with primary amines, which resulted in the preparation of 1,3-disubstituted urea without isolation formate reaction medium subjected to cyclization in the presence of alkali

KEY WORDS: CYCLIZATION, AMINOESTER, BENZO[H]QUINAZOLINE, SUBSTITUTION

INTRODUCTION

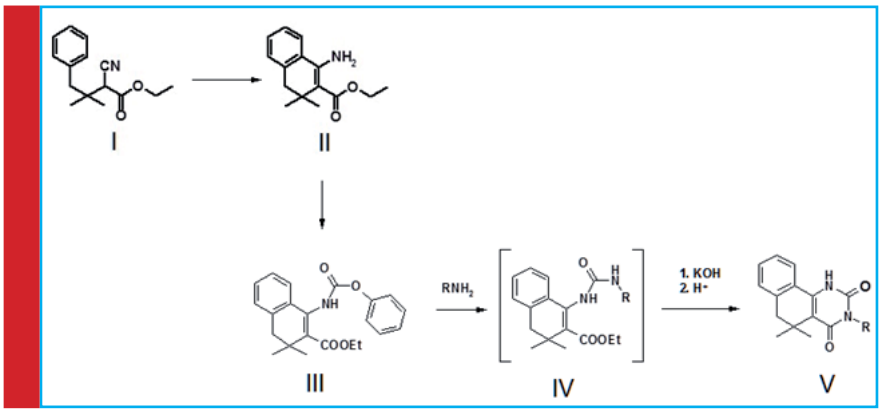
For this, ethyl 2-cyano-3,3-dimethyl-4- phenyl-butanoate(I)in H_2SO_4 solution was cyclized into 1-amino-3,3-dimethyl-3,4-dihydronaphthalene-2-ethylcarboxyiate(II), which was then reacted with chlorophenylformate (III)a method for the synthesis of 3-substituted 5,5-dimethyl-5,6-dihydrobenzo[h]quinazoline(1H,3H)2,4-dione. (IV) was developed. The method is based on the interaction of carbamate (II) with primary amines, which resulted in the preparation of 1,3-disubstituted urea without isolation formate reaction medium subjected to cyclization in the presence of alkali (Graddon & Nickel, 2012; Kwatkowski & Trojanowski, 2010)

ARTICLE INFORMATION:

**Corresponding Author: najmetorshirzad@yahoo.com*
Received 11th Dec, 2016
Accepted after revision 19th March, 2017
BBRC Print ISSN: 0974-6455
Online ISSN: 2321-4007
Thomson Reuters ISI ESC and Crossref Indexed Journal
NAAS Journal Score 2017: 4.31 Cosmos IF : 4.006

Online Contents Available at: http//www.bbrc.in/

METHODOLOGY



IV: R=NH_2;VII:R=CH_3; VIII: R=C_2H_5; IX: R=C_3H_7; X: R=izo-C_3H_7; XI: R=C_4H_9;
XI: R=cyclopentyl; XII: R=cyclohegzil; XIII: R=2-furfuryl; XIV: R=C_6H_5;
XV: R=$CH_2C_6H_5$; XVI:R=$CH_2CH_2C_6H_5$.

EXPERIMENTAL CHEMICAL PART

IR spectra were taken in mineral oil UR-20 and FT-IR Nexus instrument. PMR spectra, with or HMDS internal standard on a Varian Mercury-300 spectrometer (USA)

Table 1. 3-substituted-5,5-dimethyl-5,6-dihydrobenzo[h]quinazolin-(1H,3H)2,4-dions

Compound	R	Yield, %	Mp,° C	Rf*	Theoretical, %			experimental, %		
					C	H	N	C	C	N
22	NH_2	96	228-230	0.43 (a)	65.48	5.97	16.50	65.33	5.88	16.32
23	CH_3	43	>250	0.67 (a)	70.44	6.39	11.12	70.29	6.29	10.93
24	C_2H_5	63	230-232	0.75 (B)	71.25	6.86	10.24	71.09	6.71	10.36
25	C_3H_7	63	228-230	0.78 (a)	71.97	7.23	9.70	71.81	7.09	9.85
26	ISO-C_3H_7	56	219-220	0.76 (δ)	71.88	7.19	10.01	71.81	7.09	9.85
27	C_4H_9	83	180-182	0.53 (δ)	72.59	7.56	9.57	72.46	7.43	9.39
28	Cyclopentyl	70	>250	0.56 (π)	73.68	7.32	9.18	73.52	7.14	9.03
29	Cyclohexane	68	238-240	0.80 (r)	73.95	7.62	8.77	74.04	7.46	8.64
30	2-Furfuryl	68	219-220	0.71 (a)	70.86	5.77	8.50	70.79	5.63	8.69
31	C_6H_5	94	>250	0.69 (a)	75.64	5.56	8.63	75.45	5.70	8.80
32	$CH_2C_6H_5$	78	218-220	0.58 (π)	75.95	6.22	8.58	75.88	6.06	8.43
33	$CH_2CH_2C_6H_5$	81	>250	0.73 (a)	76.43	6.57	7.95	76.28	6.40	8.09
34	3-ClC_6H_4	55	>250	0.76 (δ)	67.93	5.01	7.82	68.09	4.86	7.94

TLC using Acetate:Benzen (1:2)

.Mass spectra were obtained on an MX-1321A spectrometer (USSR) using direct sample introduction into the ion source. TLC was carried out on Silufol R plates with detection by I_2 vapor (Patel & Woods, 2001).

1-Amino-3,3-dimethyl-3,4-dihydronaphthalene-2-ethylcarboxylate(II)

Compound I (50g,0.193mol) was placed into a 250-mL flask, stirred at 10-15°C, treated in portions with conc. H_2SO_4 (100mL), stirred at the same temperature for 7 h, neutralized with aqueous NH_4OH, and extracted with Et2O(500 mL). The extract was washed twice with H2O and dried over anhydrous Na_2SO_4. The solvent was distilled off. The solid was crystallized. The crystals were washed with EtOH(70%) and dried in air to afford II, 23g(46%yield), MP 58-60°c,Rf 0.67 (isooctane-ethylacetate,2:1) IR spectrum, v, cm-1: 1600 (c=c atom) , 1643 (c=o), 3334, 3438(NH_2). PMR spectrum (DMSO-d_6), δ, ppm:1.16 (s, 6H, 2× CH_3), 1.33 (t, J 7.1 Hz, 3H, OCH_2CH_3), 2.60 (s, 2H, 4-CH_2), 4.17 (q, J 7.1 Hz, 2H, OCH_2), 7.10 (m, 3H, 5-CH, NH_2), 7.20 – 7.28 (m, 2H, 6-CH, 7-CH), 7.59 (m, 1H, 8-CH) (Popp et al., 2006).

ETHYL–3,3–DIMETHYL–1–((PHENOXYCARBONYL) AMINO)–3,4–DIHYDRONAPHTALIN–2–CARBOXYL (III)

A mixture of II (24.5g, 0.1 moL), chlorophenyl formate (15.6 g, 0.1 mol) and Benzen (150 mol) was refluxed for 20h. The resulting crystals were filtered off, washed with H_2O, and crystallized from EtOH and wather (3:1) to afford (III) 31.5 gr (86.2% yield), mp 122-124°c, Rf 0.76 (Ethyl Acetate – Benzen, 1:2) IR spectrum, V, cm-1 :1600 (c=c arom), 1625 (c=c ethylen), 1710 (c=o), 1750 (NH). PMR spectrum (DMSO-d6)δ, ppm : 9.10 (bs, 1H, NH) (Sahai & Singh, 1998).

3–Substituted 5, 5–dimethyl– 5, 6–dihydrobenzo [h] quinazolin–(1h, 3h) 2,4–dions (v)

A mixture of carbamate (III) (3.65 gr, 0.01 mol), primary amine (0.01 mol) and ethanol (20 ml) was refluxed for 7 h , treated with KOH solution (1.1 gr 0.02 mol) in H_2O (10 ml), refluxed for another 3 h, cooled, stirred, and acidified with HCL solution (18%) to PH 3.0 – 3.5. The resulting crystals were filtered off, washed with H_2O and recrystallized from EtOH to afford (IV - XVI), MP >250 °C, R_f 0.74 (benzoyl ethyl acetate, 2:1). IR spectrum: ν, CM^{-1}: 1605 (C=Carom.); 1646 (C=C-C=O); 1711 (C=O); 3240 (NH). ^{1}HPMR spectrum (DMSO -d_6), δ, ppm, Hz: 1.28 (6H, c, $2CH_3$); 2.76 (2H, c, 6-CH_2); 7.14-7.51 (5H, m, arom.); 7.93 (1H,dd, J_1=7.7, J_2=1.2, 10-CH); 11.24 (1H, c, NH).

REFERENCES

Graddon, D.P.; Heng, K.B. Nickel.(2010) Complexes of Some 3-Substituted Pentane-2,4-diones. Aust. J. Chem. 2012, 25, 2247-2250.

Kwatkowski, E.; Trojanowski, H. Complexes of Tertiary Amides with Acetylacetonates of Oxovanadium(IV) and Copper(II) in Methylene Chloride Solution. J. Inorg. Nucl. Chem. 37, 979-983.

Patel, K.S.; Woods, J.A.O. (2001) Preparation and Physicochemical Studies of Some 3-substituted 2,4-Pentanedionatocopper(II) Complexes and their Adducts. Synth. React. Inorg. Met.-Org. Chem 20, 97-109, and references therein.

Popp, C.J.; Nelson, J.H.; Ragsdale, R.O.(2006) Thermodynamic and Infrared Studies of Tertiary Amine Oxides with Bis(2,4-Pentanedionato) oxovanadium(IV). J. Amer. Chem. Soc. 91, 610-614.

Sahai, R.; Singh, P.R.(1998) Spectroscopic Studies in Metal b-Diketonates I: Preparation and Study of Halogenated Metal Acetylacetonates. Aust. J. Chem. 20, 639-648.