Solid phase synthesis of novel pyrazole derivatives from diaryl 1,3-diketones under microwave irradiation

Suresh Singh Chauhan, A. Sharma, S. Saingar and Y. C. Joshi*

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

E-mail : sureshsingh76@yahoo.com

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Microwave irradiation is increasingly being used to accelerate the rate of reaction¹. In this paper we wish to report, reaction of diaryl-1,3-diketone² (**1a-l**) with hydrazine on silica gel under microwave irradiation to generate novel pyrazole derivatives.

Microwave irradiation of propane-1-(1,3-benzodioxol-5-yl)-3-phenyl-1,3-dione (**1a-l**) with hydrazine hydrate on silica gel gives Schiff bases type compound having novel pyrazole nucleus. Hydrazine hydrate promote the enol form of mentioned diketone. The structure of the solid phase synthesized compound are well supported by spectroscopic data (Scheme 1, Table 1).

Scheme 1

Results and discussion

In IR spectra, characteristic -NH stretching vibration was observed around 3250 cm⁻¹, -CN stretching band around 1420 cm⁻¹, symmetric and asymmetric vibration bands appearing in the region 1020–1075 and 1265–1235 cm⁻¹ respectively. In ¹H NMR all the solid phase synthesized compounds exhibit a single sharp peak in the region δ

7.21–7.34 due -NH proton. A singlet at δ 5.98–6.01 is due to dioxymethylene group. Multiplets at δ 6.6–8.3 indicates the presence aromatic protons. A singlet at δ 3.79 is observed due to the -OCH₃ group protons. ¹H NMR data of the title compound and ¹³C NMR data are presented in Table 1.

In the mass spectra of these title compounds (**2a-l**) shows molecular ion peaks (*m/z*). The [M+2]⁺ peaks was nearly one fourth of [M]⁺ peaks indicating the presence isotopic Cl³⁷, and the compound (**2d**) shows a cluster of peaks at *m/z* 343 and 345 corresponding to M⁺ and [M+2]⁺ respectively. M⁺ and [M+2]⁺ peaks have same intensity showing the presence of bromine. A cluster of ion peaks to [M]⁺, [M+2]⁺ at 298, 300 were observed in case (**2c**).

The ¹³C NMR data for the compound (**2a-l**) are presented in Table 1, and these data are in good agreement with their structure.

Experimental

Melting points are uncorrected. The IR spectra were recorded in KBr disk on a Nicolet Magna-FT-IR 550 spectrometer. ¹H NMR and ¹³C NMR were recorded on model DRX 300 at 300.13 and 75.48 MHz, respectively, in CDCl₃/DMSO-*d*₆ using TMS as internal standard. Mass spectra were recorded on Jeol D-300 spectrometer. The purity of the newly synthesized compounds were checked by TLC.

Generalized preparation of pyrazole derivatives :

Hydrazine hydrate (130 mg, 4 mmol), silica gel (2 g) and diaryl-1,3-diketone **1a-l** (2 mmol) were mixed in a mortar then transferred in to a beaker and irradiated for 2 min. The progress of reaction were monitored by TLC (CHCl₃ : CH₃OH, 9 : 1) as mobile phase. The mixture was extracted into CHCl₃ then filtered and washed with water, after drying, the organic phase was removed by a rotary evaporator.

Note

Table 1. Characterization data of title compounds

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Compd	Molecular formula	Molecular weight	¹ H NMR (δ ppm)						¹³ C NMR						M p (°C) Rep	Yield (%)			
			Ar-x	-NH 1H (s) (broad)	Methine 1H (s)	OC H ₂ O	Aromatic protons			Ar-x	OC(O)	>C=N		H			Ar at C ₁ -	Ar at C ₂ -	
2a	C ₁₆ H ₁₀ N ₂ O ₂ Cl ₂	333	-	7.31	6.76	6.02		6.90-7.99			-	101.4	150.4	136.0	97.0	142.3-	147.5-	105/ 94	
2b	C ₁₆ H ₁₀ N ₂ O ₂ Br ₂	421	-	7.28	6.79	6.02		6.92-7.83			-	101.7	151.0	135.7	97.8	140.1-	147.4-	118/ 87	
2c	C ₁₆ H ₁₀ N ₂ O ₄	324	3.79 6H, s	7.34	6.75	6.05		6.93-8.32			O-CH ₃ - 55.2	101.5	150.6	136.3	97.7	153.6-	147.6-	123/ 143/ 91	
2d	C ₁₆ H ₁₀ N ₂ O ₂ N ₂	264	-	7.37	6.70	6.00		5H-M			7.25	6.87	7.31-7.37		98.4	132.0-	147.4-	141/ 122/ 95	
2e	C ₁₇ H ₁₄ N ₂ O ₂	278	2.37, 3H, s	7.36	6.69	5.98	7.22	7.66	7.26	6.86	7.29-7.33	CH ₃ - 20.6	100.5	150.0	135.4	97.1	137.0-	147.3-	173/ 176/ 93
2f	C ₁₆ H ₁₁ N ₂ O ₂ Cl	298.5	-	7.27	6.63	6.00	7.27	7.67	7.25	6.87	7.28-7.29	-	100.6	150.0	134.9	98.3	130.6-	147.3-	116/ 112/ 89
2g	C ₁₆ H ₁₁ N ₂ O ₂ Br	343	-	7.35	6.71	6.00	7.55	7.69	7.24	6.88	7.28-7.29	-	100.6	149.8	134.2	98.6	132.2-	147.2-	128/ 130/ 92
2h	C ₁₇ H ₁₄ N ₂ O ₄	294	3.85 3H, s	7.26	6.66	6.01	6.96	7.62	7.21	6.88	7.22-7.23	OCH ₃ - 54.8	100.4	149.8	135.1	97.9	158.9-	147.4-	149/ 146/ 96
2i	C ₁₆ H ₁₂ N ₂ O ₄	280	4.05 1H, s	7.35	6.67	6.00	6.93	7.96	7.22	6.86	7.24-7.26	-	100.2	150.1	134.7	98.4	161.8-	147.4-	157/ 161/ 90
2j	C ₁₆ H ₁₄ N ₂ O ₂	279	4.81(b) 2H, s	7.29	6.66	6.01	6.69	7.90	7.22	6.88	7.23-7.25	-	100.5	149.9	135.0	98.4	151.5-	147.3-	161/ 101/ 85
2k	C ₁₆ H ₁₄ N ₂ O ₄	309	-	7.31	6.68	6.00	8.11	8.36	7.26	6.88	7.08-7.31	-	100.6	151.6	134.8	97.8	152.3-	147.4-	105/ 123/ 87
2l	C ₁₆ H ₁₆ N ₂ O ₂	308	1.76 (3H, t, J 7 Hz)	7.28	6.66	5.98	6.99	7.66	7.24	6.87	7.22-7.23	OCH ₃ - 63.2	100.3	149.9	134.8	98.2	162.3-	147.4-	152/ 149/ 92
		3.92 (2H, q, J 7 Hz)										CH ₃ - 14.7				114.3	105.7		

Further purification by column chromatography (CHCl_3 as eluent) and recrystallization gave the desired products.

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