SYNTHESIS AND SPECTRAL STUDIES OF SOME NOVEL DIALKYL / DIARYL β-DIKETONES AND β-KETOESTERS FROM DIAZONIUM SALT OF 3N-PROPYL-4-AMINO-5-CARBOXAMIDO-N-METHYL PYRAZOLE

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Abstract : Various novel β-diketones and β-ketoesters (4a-4e) has been prepared by the condensation of diazonium salt of 3n-propyl-4-amino-5-carboxamido-N-methyl pyrazole with β-diketones and β-ketoesters (3a-3e). Structures of these compounds were established on the basis of elemental analysis, IR, ^{1}H NMR and ^{13}C NMR spectral studies

Introduction

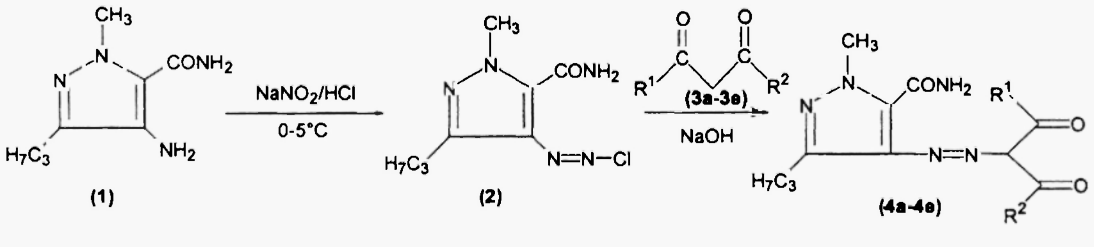
β-Diketones and β-ketoesters serve as precursors for the synthesis of various biologically active heterocyclic compounds such as diazepines[1], benzodiazepines[2], benzothiazepines[3], benzothiazines[4], pyrazoles[5], imidazoles and benzimidazoles[6].

Pyrazole moiety have significant pharmacological properties. They show antimicrobial[7], anti-inflammatory[8], antiviral[9] and pesticidal activity[10]. Substituted pyrazoles are useful as cardiovascular[11], antitumor[12] and some hypolipemic activity. It is interesting to note that pyrazoles are reported as well known pharmaceuticals.[13-15]

Unusual and mainfold biologically important derivatives of pyrazole moiety developed our interest to synthesize some novel biologically active β-diketones and β-ketoesters.

Result and Discussion

The diazonium salt of 3n-propyl-4-amino-5-carboxamido-N-methyl pyrazole was condensed with β-diketones and β-ketoesters in the presence of NaOH with continuous stirring at 60°C for 6 hours (Scheme-1). The products so obtained were characterized on the basis of various spectral studies viz. IR, ^{1}H NMR and ^{13}C NMR (Scheme-1, Tables 1-4).



4a : $R^1 = -CH_3$ $R^2 = -CH_3$ 4b : $R^1 = -CH_3$ $R^2 = -OC_2H_5$
4c : $R^1 = -C_6H_5$ $R^2 = -C_6H_5$ 4d : $R^1 = -CH_3$ $R^2 = -C_6H_5$
4e : $R^1 = -OC_2H_5$ $R^2 = OC_2H_5$

Scheme-1

Table-1 : Elemental Analysis of Title Compounds

Compd.	M.F.	M.W.	Calculated (Found)			M.P. (°C)
			C	H	N	
4a	$C_{13}H_{19}N_5O_3$	293	53.24 (52.58)	6.48 (5.99)	23.89 (24.01)	170°C
4b	$C_{14}H_{21}N_5O_4$	323	52.01 (52.3)	6.50 (6.28)	21.16 (21.05)	142°C
4c	$C_{23}H_{28}N_5O_3$	422	65.40 (65.22)	6.63 (6.34)	16.58 (15.75)	168°C
4d	$C_{18}H_{21}N_5O_3$	355	60.84 (59.79)	5.91 (6.02)	19.17 (20.01)	154°C
4e	$C_{15}H_{23}N_5O_3$	353	50.99 (50.38)	6.51 (6.69)	19.83 (20.01)	138°C

Spectral Studies

In IR spectra, a sharp band at 1720 cm^{-1} accounted for the $-\overset{\overset{O}{\|}}{C}-$ (β-diketones) stretching vibration and absorption band between 3100-3000 cm^{-1} is due to C–H stretching was observed.

Symmetric and asymmetric $-CONH_2$ (primary amide) stretching vibrations were observed at 3400 cm^{-1} and 3500 cm^{-1} respectively and in – $CONH_2$ group $-\overset{\overset{O}{\|}}{C}-$ stretching vibration band observed at 1680 cm^{-1}.

In ^1H NMR, a peak is observed at δ2.5-2.8 which accounted for the proton of β-diketones and β-ketoesters and a peak observed at δ14.96 due to enolic form. A broad singlet at δ 8.00 is due to amide group and a singlet at δ 3.69 due to $N\text{-}CH_3$ group.

A triplet at δ1.02 ($CH_2CH_2\mathbf{CH_3}$), sextet δ1.85 ($-CH_2-\mathbf{CH_2}CH_3$) and triplet at δ2.85 due to ($\mathbf{CH_2}CH_2CH_3$) was observed.

The IR, ^1H NMR and ^{13}C NMR data are tabulated in table 2,3 and 4.

Table-2 : IR spectra data (cm^{-1}) of β-diketones and β-ketoesters (4a-4e)

Compd.	–C–H	$-\overset{\overset{O}{\|}}{C}-$	N–H	$-\underline{C}ONH_2$	–OH(enol)
4a	2930	1716	3400 3500	1680	3100
4b	2915	1716	3405 3500	1685	3100
4c	2925	1725	3400 3500	1675	3100
4d	2920	1719	3400 3500	1680	3100
4e	2920	1765	3400 3500	1685	3100

Table-3 : ^1H NMR spectral data (δ ppm) of β-diketones and b-ketoester (4a-4e)

Compd.	$CH_3-\overset{\overset{O}{\|}}{C}-$	>C–H	$\overset{\overset{O}{\|}}{C}-OCH_2CH_3$	Ar-H	$N-CH_3$	$-CONH_2$	$CH_2CH_2CH_3$	–OH (enol)
4a	2.5 (3H, s)	7.2	-	-	4.28 (3H, s)	8.1 (2H, s)	1.02 (t) 1.85 (m) 2.90 (t)	14.90
4b	2.8 (3H, s)	7.12	1.64 (t) 4.42 (q)	-	4.28 (3H, s)	8.19 (2H, s)	1.02 (t) 1.85 (m) 2.90 (t)	14.98
4c	-	7.13	-	7.36 (5H, s)	4.29 (3H, s)	8.20 (2H, s)	1.02 (t) 1.85 (m) 2.90 (t)	14.85
4d	2.65 (3H, s)	7.15	-	7.28 (5H, s)	4.28 (3H, s)	8.15 (2H, s)	1.02 (t) 1.85 (m) 2.90 (t)	14.86
4e	-	7.25	1.64 (t) 4.42 (q)	-	4.28 (3H, s)	8.16 (2H, s)	1.02 (t) 1.85 (m) 2.90 (t)	15.00

Table-4 : ^{13}C NMR data of the title compound (in ppm)

Compd.	$N-CH_3$	$CH_2CH_2CH_3$	$CH_3-\overset{\overset{O}{\|}}{C}-$	$-\overset{\overset{O}{\|}}{C}-OCH_2CH_3$	$-\overset{\overset{O}{\|}}{C}-Ar$	$-\overset{\overset{O}{\|}}{C}-NH_2$	>CH–
4a	65.4	15.8, 29.2, 40.3	195	-	-	160	148
4b	65.4	15.8, 29.2, 40.3	195	167.5	-	160	148
4c	65.4	15.8, 29.2, 40.3	-	-	168	162	157
4d	65.4	15.8, 29.2, 40.3	196	-	169.5	161	151
4e	65.4	15.8, 29.2, 40.3	-	169.4	-	165	152

Experimental

All melting point are uncorrected. The IR spectra were recorded in KBr pellets on a Nicolet-megna-FT-IR550 spectrometer. ^1H NMR and ^{13}C NMR were recorded on model DRX 300 at 300.13 and 75.48 MHz-respectively, in $CDCl_3$/DMSO-d_6 using TMS as internal standard. The purity of the newly synthesized compounds were checked by TLC.

General method of preparation of β-diketones and β-ketoesters (4a-4e)

The diazonium salt is condensed with β-diketones and β-ketoesters (3a-3e) in presence of NaOH by continuously stirring the reaction mixture for 6-8 hours at 60°C. The progress of the reaction was monitored intervally through TLC. After the completion of the reaction, the reaction mass was poured in crude ice and acidified and dried in vaccum. The obtained product was crystalized in chloroform. Purity of the products was checked through TLC using 7:2:1 (Benzene : ethanol : ammonia) upper layer as mobile phase.

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