

REACTION OF 4-AMINO-4,5-DIHYDRO-1*H*-1,2,4-TRIAZOL-5-ONES WITH 2,5-DIMETHOXYTETRAHYDROFURAN

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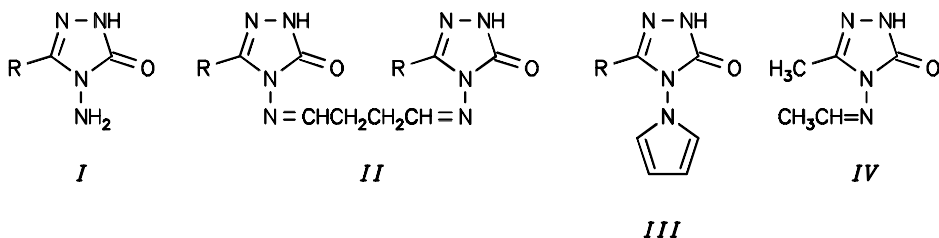
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A number of studies involving some reactions of 4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-ones have been made in recent years¹⁻⁶. On the other hand, the reactions of some *N*-aminoheteroaryls with 1,4-diketones or 1,4-dialdehydes to give *N,N'*-linked biheteroaryls have also been reported⁷⁻¹⁰. In the present study, a series of 3-alkyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-ones *I* were condensed in good yields with the succinaldehyde equivalent, 2,5-dimethoxytetrahydrofuran to give *N,N'*-bis(3-alkyl-4,5-dihydro-1*H*-1,2,4-triazol-5-on-4-yl)-1,4-butanediimines *II* or 1-(3-alkyl-4,5-dihydro-1*H*-1,2,4-triazol-5-on-4-yl)pyrroles *III* in nitrobenzene or acetic acid medium, respectively. To obtain more information on type *II* compounds, 3-methyl-4-ethyliden-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one (*IV*) was synthesized.

EXPERIMENTAL

Melting points were determined on a Büchi oil heated melting point apparatus and are uncorrected. Experimental data for compounds *II*, *III* and *IV* are given in Table I. Infrared spectra (given in cm^{-1})



In formulae *I* - *III* :

- a**, R = CH₃; **b**, R = CH₃CH₂; **c**, R = C₆H₅CH₂;
d, R = *p*-MeC₆H₄CH₂; **e**, R = *p*-ClC₆H₄CH₂; **f**, R = *p*-NO₂C₆H₄CH₂;
g, R = C₆H₅; **h**, R = *p*-MeC₆H₄

TABLE I
Experimental data for compounds II, III and IV

Compound	M.p., °C Yield, %	Formula M.w.	Calculated/Found		
			% C	% H	% N
<i>Ila</i>	225 ^a	C ₁₀ H ₁₄ N ₈ O ₂	43.16	5.07	40.27
	63	278.3	42.94	5.13	40.00
<i>Ilb</i>	221 ^a	C ₁₂ H ₁₈ N ₈ O ₂	47.05	5.92	36.58
	69	306.3	46.79	5.95	36.74
<i>Ilc</i>	228 ^a	C ₂₂ H ₂₂ N ₈ O ₂	61.38	5.15	26.03
	78	430.5	61.25	5.12	25.94
<i>Ild</i>	247 ^a	C ₂₄ H ₂₆ N ₈ O ₂	62.87	5.71	24.44
	65	458.5	62.60	5.77	24.14
<i>Ile</i>	250 ^a	C ₂₂ H ₂₀ Cl ₂ N ₈ O ₂	52.91	4.04	22.44
	63	499.4	52.86	4.22	22.29
<i>Ilf</i>	265 ^a	C ₂₂ H ₂₀ N ₁₀ O ₆	50.77	3.87	26.91
	79	520.5	50.66	3.90	26.86
<i>Ilg</i>	230 ^b	C ₂₀ H ₁₈ N ₈ O ₂	59.69	4.51	27.84
	71	402.4	59.40	4.78	27.60
<i>IIh</i>	307 ^c	C ₂₂ H ₂₂ N ₈ O ₂	61.38	5.15	26.03
	83	430.5	61.10	5.09	25.73
<i>IIIa</i>	135 ^b	C ₇ H ₈ N ₄ O	51.21	4.91	34.13
	76	164.2	51.34	4.87	34.41
<i>IIIc</i>	164 ^d	C ₁₃ H ₁₂ N ₄ O	64.98	5.03	23.32
	88	290.3	64.76	5.10	23.37
<i>IIId</i>	190 ^d	C ₁₄ H ₁₄ N ₄ O	66.12	5.55	22.04
	89	254.3	66.00	5.50	21.85
<i>IIIe</i>	191 ^e	C ₁₃ H ₁₁ ClN ₄ O	56.84	4.03	20.39
	86	274.7	57.13	4.08	20.56
<i>IIIg</i>	204 ^b	C ₁₂ H ₁₀ N ₄ O	63.70	4.46	24.77
	91	226.2	63.42	4.28	24.50
<i>IV</i>	126 ^e	C ₅ H ₈ N ₄ O	42.85	5.75	39.98
	41	140.1	42.60	5.85	39.96

Crystallized from: ^a Ethanol; ^b benzene-petroleum ether (1 : 1); ^c DMSO-H₂O (1 : 3); ^d water; ^e benzene.

TABLE II
IR Data for compounds *II*, *III* and *IV*

Compound	ν_{NH}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	Substituted benzenoid ring
<i>Ila</i>	3 175	1 690	1 590	–
<i>Ilb</i>	3 180	1 695	1 580	–
<i>Ilc</i>	3 170	1 700	1 582	730, 695
<i>Ild</i>	3 185	1 685	1 590	810
<i>Ile</i>	3 175	1 695	1 590	825
<i>Ilf</i>	3 175	1 692	1 585	808
<i>Ilg</i>	3 190	1 690	1 575	760, 690
<i>IIh</i>	3 170	1 695	1 575	820
<i>IIIa</i>	3 200	1 710	1 595	–
<i>IIIc</i>	3 195	1 705	1 590	730, 690
<i>IIId</i>	3 200	1 695	1 588	800
<i>IIIe</i>	3 195	1 695	1 590	815
<i>IIIg</i>	3 190	1 705	1 580	765, 690
<i>IV</i>	3 190	1 690	1 595	–

TABLE III
 ^1H NMR Data for compounds *II*

Compound	2 CH ₃	CH ₂ CH ₂	2 CH ₂	2 CH	2 NH	Aromatic H
<i>Ila</i>	2.22 s	2.40 – 3.00 m	–	9.20 s	12.00 s	–
<i>Ilb</i>	1.16 t	^a	^a	9.15 s	11.95 s	–
<i>Ilc</i>	–	2.35 – 2.85 m	3.85 s	9.05 s	11.90 s	7.20 s, 10 H
<i>Ild</i>	2.20 s	2.40 – 2.90 m	3.85 s	9.00 s	11.90 s	7.10 s, 8 H
<i>Ile</i>	–	2.40 – 2.85 m	3.90 s	9.15 s	12.05 s	7.30 s, 8 H
<i>Ilf</i>	–	2.35 – 2.80 m	4.05 s	9.16 s	12.18 s	7.60 d, 4 H 8.25 d, 4 H
<i>Ilg</i>	–	2.40 – 3.05 m	–	9.16 s	12.20 s	7.40 – 8.20 m, 10 H
<i>IIh</i>	3.10 s	2.30 – 2.80 m	–	9.05 s	12.10 s	7.32 d, 4 H 7.76 d, 4 H

^a 2.20 – 2.90 m, 8 H (4 CH₂).

were run as potassium bromide pellets using a Perkin–Elmer 337 spectrophotometer (Table II). ^1H NMR and ^{13}C NMR spectra (given in δ , ppm) were recorded on a Varian A60 spectrometer or a Bruker AC-200 FT instrument in $(\text{CD}_3)_2\text{SO}$. Combustion analyses were performed on a Carlo Erba 1106 elemental analyzer. ^1H NMR Data are given in Tables III and IV. Mass spectrum of compound *Ia* was run on a Kratos MS-50 instrument. The starting compounds *I* were synthesized by methods described earlier^{2,11}.

N,N'-Bis(3-alkyl-4,5-dihydro-1*H*-1,2,4-triazol-5-on-4-yl)-1,4-butanediimines *II*.

General Procedure

3-Alkyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one (*I*, 0.01 mol) was treated with a solution of 2,5-dimethoxytetrahydrofuran (1.3 ml, 0.01 mol) in nitrobenzene (20 ml), and the mixture was refluxed for 2 h. After cooling, the precipitate formed was recrystallized from an appropriate solvent to give compound *II*.

1-(3-Alkyl-4,5-dihydro-1*H*-1,2,4-triazol-5-on-4-yl)pyrroles *III*.

General Procedure

3-Alkyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one (*I*, 0.01 mol) was dissolved in acetic acid (25 ml) and treated with 2,5-dimethoxytetrahydrofuran (1.3 ml, 0.01 mol). The mixture was refluxed for 1.5 h and then evaporated at 50 – 55 °C under reduced pressure. Several recrystallizations of the residue from an appropriate solvent afforded pure compound *III*.

Synthesis of 3-Methyl-4-ethylideneamino-4,5-dihydro-1*H*-1,2,4-triazol-5-one (*IV*)

3-Methyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one (*Ia*) (1.14 g, 0.01 mol) was dissolved in ethanol (30 ml), and acetaldehyde (0.62 ml, 0.11 mol) was added to the solution. The mixture was refluxed for 1 h and then evaporated at 25 – 30 °C under reduced pressure. The viscous residue

TABLE IV
 ^1H NMR Data for compounds *III* and *IV*

Compound	CH_3	CH_3	CH_2	CH	NH	Aromatic H
<i>IIIa</i>	2.02 s	–	–	–	12.05 s	6.26 t, 2 H; 7.00 t, 2 H
<i>IIIc</i>	–	–	3.95 s	–	12.15 s	6.20 t, 2 H; 6.90 t, 2 H 7.00 – 7.40 m, 5 H
<i>III d</i>	2.34 s	–	3.85 s	–	12.25 s	6.30 t, 2 H; 6.95 t, 2 H 7.20 q, 4 H
<i>IIIe</i>	–	–	3.90 s	–	12.20 s	6.20 t, 2 H; 6.90 t, 2 H 7.20 q, 4 H
<i>IIIg</i>	–	–	–	–	12.40 s	6.30 t, 2 H; 7.10 t, 2 H; 7.30 – 7.60 m, 5 H
<i>IV</i> ^a	2.10 d	2.28 s	–	9.15 s	12.30 s	–

^a CDCl_3 .

solidified in deep-freeze with 2 – 3 ml of ethyl acetate. Recrystallization of the product from benzene gave pure compound *IV*. The ^{13}C NMR data for compounds *Ila* and *Ilc* are given below.

Ila: 158.88 (2 C, C=N), 151.24 (2 C, triazole C₅), 143.87 (2 C, triazole C₃), 28.77 (2 C, CH₂CH₂), 10.95 (2 C, CH₃).

Ilc: 158.72 (2 C, C=N), 151.30 (2 C, triazole C₅), 145.87 (2 C, triazole C₃), 135.69 (2 C, aryl ring carbons), 128.66 (4 C, aryl ring carbons), 128.31 (4 C, aryl ring carbons), 126.60 (2 C, aryl ring carbons), 30.91 (2 C, CH₂), 28.25 (2 C, CH₂CH₂).

Molecular ion (M^+) for compound *Ila*: 278.

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