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5,7-DIARYL-5,6-DIHYDRO-4H-TETRAZOLO[1,5-b]-1,2,4-TRIAZEPINES

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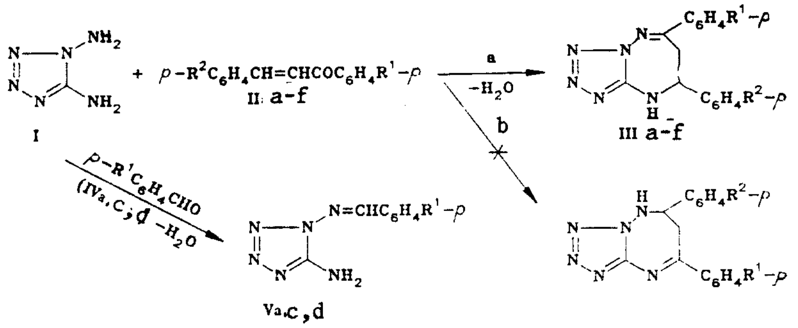
Cyclocondensation of 1,5-diaminotetrazole with chalcones has given aryl-5,6-dihydro-4H-tetrazolo[1,5-b]-1,2,4-triazepines.

The purpose of this investigation was to examine the cyclocondensation of 1,5-diaminotetrazole (I) with aromatic α,β-unsaturated ketones (chalcones). The reduced nucleophilicity of (I) resulted in the failure of attempts to carry out the condensation, either under mild conditions [1-3], or by boiling in triethylamine or acetic acid. 1,5-Diaminotetrazole reacted with the chalcones (IIa-f) on boiling in DMF for ~3 h. The sole cyclocondensation products were the compounds (IIIa-f), which according to their elemental analyses and spectral properties (Tables 1 and 2) were dihydrotetrazolotriazepines, no cleavage of the "hydrazine" amino group, such as occurs with 1,2-diaminobenzimidazole [4], being observed.



II—V a,e,f $R^1=H$, b $R^1=CH_3$, c $R^1=OCH_3$, d $R^1=NO_2$; a—d $R^2=H$, e $R^2=CH_3$, f $R^2=Cl$

In the IR spectra of (IIIa-f), $\nu_{C=N}$ and ν_{NH} absorptions were reliably identified at 1620-1632 and 3405-3483 cm^{-1}, respectively (Table 1). The PMR spectra of these compounds showed (Table 2), in addition to multiplets for the aromatic protons and a singlet for the methyl groups [in the case of (IIIb, c, e)], signals for the NH group and three quartets attributed to the protons of the CH–CH$_2$ fragment. The mass spectrum of (IIIa) showed a strong (13%) molecular ion peak, m/z 290, further fragmentation involving cleavage in one sequence or another of a molecule of nitrogen or HN$_3$, HCN, benzonitrile, stilbene, or phenylacetylene (see Experimental).

The nonequivalence of the amino groups in 1,5-diaminotetrazole makes it possible for dihydrotriazepine ring formation to occur by either of two routes (a and b). 1-Aminotetrazole is known [5] to readily afford a Schiff base, whereas 5-aminotetra-

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TABLE 1. Properties of (IIIa-f) and (Va, c, d)

Compound	Empirical formula	mp, °C (decomp.)	IR spectrum (KBr), ν, cm^{-1}		UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	Yield, %
			C=N	NH		
IIIa	$C_{16}H_{14}N_6$	227	1620	3413	309 (18,2)	55
IIIb	$C_{17}H_{16}N_6$	224...225	1620	3425	312 (18,0)	55
IIIc	$C_{17}H_{16}N_6O$	247	1632	3416	315 (19,1)	55
IIId	$C_{16}H_{13}N_7O$	251...253	1634	3436	342 (18,8)	45
IIIe	$C_{17}H_{16}N_6$	213	1622	3483	309 (18,5)	37
IIIf	$C_{16}H_{13}ClN_6$	249...251	1624	3405	310 (18,3)	50
Va	$C_8H_8N_6$	224*	1656	3405, 3505**	305 (18,3)	82
Vc	$C_9H_{10}N_6O$	228	1650	3390, 3485**	318 (18,8)	90
Vd	$C_8H_7N_7O_2$	224...225	1648	3395, 3497**	324 (17,9)	90

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*According to [5], mp 225-226°C.

**ν_{NH_2} in CCl_4.

TABLE 2. PMR Spectra of (IIIa-f) (in DMSO-D_6)

Compound	Chemical shifts, ppm*					Coupling constants, Hz		
	CH_3, s	CH_2		CH, dd	NH, s	J_{AB}	J_{AX}	J_{BX}
		H_A, dd	H_B, dd					
IIIa	—	3,30	4,02	5,56	9,90	−17,8	7,6	11,5
IIIb	2,29	3,21	3,92	5,44	9,84	−17,5	7,5	11,7
IIIc	3,75	3,19	3,93	5,41	9,96	−17,9	7,7	11,4
IIId	—	3,20	4,00	5,62	9,80	−18,0	7,6	11,2
IIIe	2,20	3,19	3,92	6,41	9,82	−17,5	7,5	11,1
IIIf	—	3,26	3,97	5,47	9,91	−17,5	7,6	11,3

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*The aromatic protons in (IIIa-f) resonated at 6.8-8.2 ppm.

zole does not undergo this reaction [6]. In addition, the condensation of 1,5-diaminotetrazole with carbonyl compounds also leads exclusively to the 1-arylideneamino compounds, similar behavior being seen in the formation of tetrazolotriazepine systems [5]. For these reasons, we assume that route **a** is operative.

This was confirmed by comparing the UV spectra of (IIIa, c, d) with those of the model anils (Va, c, d) (Table 1). The UV spectra of (IIIa, c, d) and (Va, c, d), which contain the same substituent R^1, are of the same type, thus confirming the identical nature of the chromophoric systems in both types of compounds. The slight differences in the λ_{max} values of comparable compounds are probably due to differences in the conformational structures of the arylideneaminotetrazole fragments. In fact, the position of the long-wavelength absorption in compounds (III) is more sensitive to the substituent R^1 than is the case in the anils (V) (Table 1). Compounds (IIIa-c, e, f) also show a blue fluorescence [λ_{max} for (IIIa), 405 nm), which is not shown by the anils (Va, c, d), nor by other annelated di- and triazepine systems [1-3], which also suggests a fairly rigid and nearly planar conformation of the arylideneaminotetrazole fragment in these compounds [7].

The δ and J values for the CH–CH_2 protons in the PMR spectra are substantially the same in the series of compounds (IIIa-f) (Table 2), although they differ considerably from those of analogous compounds [1-3]. For example, in (IIIa-f) the nonequivalence of the methylene protons is much increased ($\delta_{H_A} - \delta_{H_B}$ = 0.71-0.80 ppm), and both the geminal and vicinal coupling constants of the CH–CH_2 grouping are much greater. The high absolute values for J_{AB} in the spectra of (IIIa-f) indicate that the plane of the π-electrons of the C=N bond and the H–C–H plane are nearly parallel [8]. A study of Dreiding models of the dihydrotriazepine ring shows that this orientation involves flattening of the arylideneaminotetrazole moiety in (IIIa-f), which accords well with the conclusions drawn above.

EXPERIMENTAL

The IR spectra were obtained on a Specord IR-75 in KBr disks (IIIa-f) and (Va, c, d) or in solution in CCl_4 (Va, c, d), at concentrations of $(3\text{-}5)\cdot 10^{-4}$ mole/liter. The UV spectra were obtained on a Specord UV-vis in methanol at concentrations of $(2\text{-}3)\cdot 10^{-5}$ mole/liter, and PMR spectra on a Bruker WP-200 (200 MHz) in DMSO-D_6, internal standard HMDS. The mass spectrum of (IIIa) was obtained on a Varian MAT-212, ionizing voltage 70 eV, and its fluorescence spectrum on a Hitachi 850 spectrofluorimeter. The purity of (IIIa-f) and (Va, c, d) were checked by TLC on Silufol UV-254 plates, using methanol and ethyl acetate as eluents.

Compounds (Va, c, d) were obtained from the diamine (I) and aldehydes (IVa, c, d) as described in [5].

5,7-Diphenyl-5,6-dihydro-4H-tetrazolo[1,5-b]-1,2,4-triazepine (IIIa). A solution of 0.4 g (4 mmoles) of 1,5-diaminotetrazole and 0.83 g (4 mmoles) of the chalcone in 1 ml of DMF was boiled for 3 h, then mixed with 30 ml of benzene. After cooling, the crystals of (IIIa) which separated were filtered off (0.6 g, 55%), mp 227°C (from ethanol). Mass spectrum: 290 (13), 262 (5), 247 (9), 222 (10), 221 (17), 206 (9), 191 (5), 145 (49), 144 (5), 129 (8), 119 (8), 118 (11), 117 (7), 116 (7), 115 (13), 105 (5), 104 (46), 103 (30), 91 (14), 89 (6), 79 (7), 78 (100), 77 (44), 76 (9), 63 (8).

Compounds (IIIb-f) were obtained similarly.

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