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CARBOCYCLE ANNELATED 1,2,4-TRIAZOLO[1,5-*a*]PYRIMIDINES

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UDC 547.859.1'792.3'514.472'592:
543.422'426

Reaction of 3-amino-1,2,4-triazole with mono- and dibenzalcycloalkanones gives 4,7-dihydro-1,2,4-triazolo[1,5-a]pyrimidines annelated by five-, six-, or seven-membered carbocycles. They can be dehydrogenated to the corresponding heteraromatics. The spectro-luminescent properties of the compounds obtained are discussed.

We have previously reported [1] a method for synthesis of 4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidines based on the condensation of 3-amino-1,2,4-triazole with α,β-unsaturated ketones. However, as is known [2, 3], cyclic unsaturated cyclic ketones which have a rigid s-cis structure are characterized by a sharply lowered reactivity toward many binucleophiles (hydrazine, aromatic and heteroaromatic o-diamines). Thus, the use of these ketones in the synthesis of heterocyclic systems is limited. The aim of this work was to investigate the cyclocondensation of 3-amino-1,2,4-triazole (I) with the mono- and dibenzalcycloalkanones II-IV.

Refluxing solutions of amine I and ketones II-IV for 0.5-2 h in DMF gives the annelated carbocycles of the dihydro-1,2,4-triazolo[1,5-*a*]pyrimidines V-VII. Comparison of the target compound yields and the reaction times (Table 1) as determined by us with those given in [1] points to the absence of a significant lowering of the reactivity of ketones II-IV when compared with their acyclic analogs. Thus, the condensation of 3-amino-1,2,4-triazole with α,β-unsaturated ketones is less sensitive to the geometry of the enone fragment than analogous reactions based on 1,2- and 1,4-binucleophiles [2, 3] (see scheme below).

It should be mentioned that the highest reactivity among the ketones IVa-c is observed for 2-benzal-1-indanone (IVa) which requires only a 0.5-h reaction time with amine I (instead of the 1.5 h needed for ketones IVb, c). Lowering of the reac-

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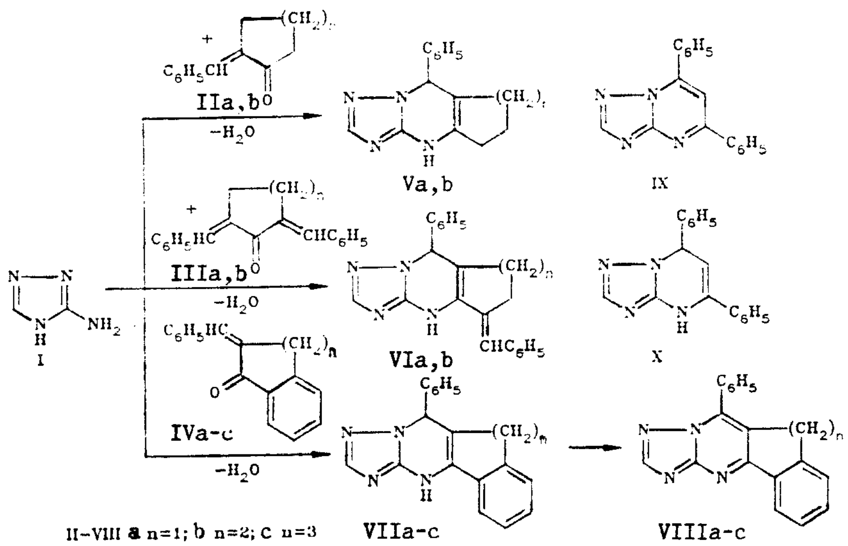

tion time to 0.5 h for IVb, c leads to an approximately twofold fall in product yield. The 2-benzal-1-indanone molecule is planar [5] and significantly polarized which results in an increase in basicity and dipole moment [5] when compared with IVb, c. A marked deviation of the valence angles for the five-membered ring in IVa from normal values [4] is evidence of strain. In all, these factors probably determine the increased reactivity of ketone IVa.

In order to prepare heteroaromatic 1,2,4-triazolo[1,5-*a*]pyrimidines, which have attracted our attention as possible luminescent materials, we have also dehydrogenated VIIa-c to their heteroaryl analogs VIIIa-c.

The obtained compounds were identified by spectroscopic methods (Tables 1 and 2). Thus, the IR spectra of V-VII show a $\nu_{C=C}$ band in the region typical of 1,4-dihydropyrimidines [6]. The PMR spectra of V-VII show a multiplet for the aryl protons, signals for the $(CH_2)_n$ group and singlets for the 2-H protons and the 7-H and NH of the dihydrotriazolopyrimidine bicycle (Table 1). The high value of δ_{NH} in these spectra undoubtedly points to the acidic character of the imine protons in V-VII.

Heteroaromatization of VIIa-c leads to loss of the $\nu_{C=C}$ band in the IR and of the $H_{(7)}$ and NH protons in the PMR spectra (Table 1). Moreover, the change for VIIa to VIIIa is accompanied by a change in the PMR spectral signals characterizing the CH_2 group protons. Thus they may be diastereotopic in VIIa and form an AB-system with a spin-spin coupling typical of pentadienes, but they become equivalent in VIIIa (Table 1).

It was expected that the restricted conformational lability of the phenyl nucleus in VII and VIII would be apparent in their UV spectra and in the fluorescence spectra of VIIIa-c (V-VII are not luminescent). A comparison of the spectroluminescent properties of VII and VIII with those of 5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine IX (λ_{max} 318 nm, ε $15.0 \cdot 10^3$) and its dihydro derivative X (λ_{max} 287 nm, ε $4.5 \cdot 10^3$) [1] reveals the following features. Annelation of the carbocycle has virtually no effect on the spectra of the dihydro-1,2,4-triazolo[1,5-*a*]pyrimidines VIIa-c and X thus confirming the correctness of using planar models for the quantochemical calculations of dihydroazolopyrimidine spectral absorption [7]. By contrast, the spectra of VIIIa-c and IXa show differences in position and especially in intensity in their longwave absorption bands. A marked hypsochromic shift is observed in going from VIIIa to VIIIc and this is accompanied by a greater than twofold fall in ε (Table 1). The fluorescence spectra of VIIIa-c (Table 2) also show a hypsofluoric change in going from VIIIa to VIIIb, c with a sharp increase in the Stokes shift and a fall in the quantochemical yield for VIIIc.

These results prove a notable effect of the conformation of the annelated carbocycle on the spectral properties of VIIIa-c. The condensed system of VIIIa is certainly practically planar. The close values of the fluorescence λ_{max} for VIIIa and IX shows that, in the excited state of IX, a planar structure is also realized for the 5-phenyltriazolo[1,5-*a*]pyrimidine fragment. By contrast, the di- and trimethylene bridges probably hinder complete planarity of the π-electron systems of VIIIb, c and this is experimentally shown by the hypsofluoric shift of the luminescence band for these compounds. In addition, the high value of the Stokes shift for VIIIc points to a significant change in the geometry of the molecule upon excitation. Evidently, the conjugation of the phenyl nucleus with the remainder of the molecule is significantly disturbed in the ground state. This explains both the differences between VIIIc and VIIIa, b or IX in the UV and also the marked lowering of the fluorescence quantum yield for VIIIc.

TABLE 1. Parameters for Compounds V-VIII.

Compound	Empirical formula	Mp, °C	IR spectrum, $\nu_{C=C}$, cm^{-1} (KBr)	UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	δ, ppm, (in pyridine-D_5)					Reaction time, h	Yield, %
					NH, s	CH*, s	arom. protons, m	CH (HC=), s	$(CH_2)_n$		
Va	$C_{14}H_{14}N_4$	226	1692	260 (2,8)	9,08	7,88	6,90...7,10	5,64	1,60...2,50 m	1,5	61
Vb	$C_{15}H_{16}N_4$	228...230	1689	265 (3,5)	9,38	7,46	7,00...7,35	5,66	1,35...2,20 m	1,5	66
VIa	$C_{21}H_{18}N_4$	221...223	1635, 1655	269 (19,7), 311 (18,6)	8,65	7,88	7,00...7,60	6,16 (6,90)	2,10...2,90 m	2,0	65
VIb	$C_{22}H_{20}N_4$	256	1649, 1666	268 (24,8), 308 (13,4)	8,90	7,50	6,95...7,50	6,60 (6,83)	1,90...2,80 m	2,0	60
VIIa	$C_{18}H_{14}N_4$	288 decomp.	1650	290 (5,5)	8,83	7,89	6,80...7,50	6,42	3,01 d; 2,77 d ($J = -22,5$ Hz)	0,5	76
VIIb	$C_{19}H_{16}N_4$	286 decomp.	1649	290 (5,1)	8,65	8,09	7,00...7,40	6,02	1,70...2,70 m	1,5	72
VIIc	$C_{20}H_{18}N_4$	259	1662	288 (4,3)	8,96	7,99	7,00...7,30	6,09	1,20...2,60 m	1,5	75
VIIIa	$C_{18}H_{12}N_4$	240	—	323 (25,9)	—	8,66	7,20...8,20	—	3,74 s	—	70
VIIIb	$C_{19}H_{14}N_4$	266...267	—	318 (18,1)	—	8,63	7,00...7,70	—	2,50...2,80 m	—	73
VIIIc	$C_{20}H_{16}N_4$	212...213	—	301 (12,0)	—	8,60	7,05...7,70	—	2,30...2,80 m	—	80

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*Triazole ring.

TABLE 2. Luminescence Spectra of VIIIa-c, IX (in ethanol)

Compound	λ_{max}, nm	Quantum yield, %	Stokes shift, cm^{-1}
VIIIa	403	16	6146
VIIIb	387	13	5607
VIIIc	388	4	7450
IX	402	13	6570

EXPERIMENTAL

Electronic absorption spectra were measured on an M-40 spectrophotometer in ethanol at a concentration of $(2\text{-}3)\cdot 10^{-5}$ molar. Fluorescence spectra were measured on a Hitachi 850 spectrofluorimeter and IR spectra on a Specord IR-75 for KBr tablets. PMR spectra were recorded on a Tesla BS-497 instrument (100 MHz) in pyridine-D_5 with TMS as internal standard. The reaction yield and purity were monitored using TLC on Silufol UV-254 plates with acetone or chloroform as eluents.

The nitrogen content in these compounds agreed with those calculated.

The synthesis of IX and X has been described in [1].

7-Phenyl-4,7-dihydro-5,6-trimethylene-1,2,4-triazolo[1,5-*a*]pyrimidine (Va, $C_{14}H_{14}N_4$). A solution of 3-amino-1,2,4-triazole (0.84 g, 10 mmoles) and 2-benzalcyclopentanone (1.62 g, 10 mmoles) in DMF (0.5 ml) was refluxed for 1.5 h, cooled, mixed with benzene (20 ml), and filtered to give Va (1.6 g, 59%) with mp 205-207°C (from benzene-DMF, 1:1).

Compounds Vb, VIa, b, and VIIa-c were obtained similarly.

10-Phenylindeno[g]-1,2,4-triazolo[1,5-*a*]pyrimidine (VIIIa, $C_{18}H_{12}N_4$). A solution of Br_2 (0.3 g, 1.9 mmoles) in acetic acid (5 ml) was added dropwise with vigorous stirring to a solution of 7-phenyl-4,7-dihydroindano[g]-1,2,4-triazolo[1,5-*a*]pyrimidine (VIIa, 0.5 g, 1.8 mmoles) in acetic acid (15 ml). The reaction mixture was stirred for 5 min at room temperature, mixed with water (50 ml), and filtered to give VIIIa (0.35 g, 70%) with mp 240°C (from ethanol).

Compounds VIIIb, c were obtained similarly.

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