CONDENSATION OF AMINO AZOLES WITH BENZOCYCLOALKANONES AND DIMETHYLFORMAMIDE

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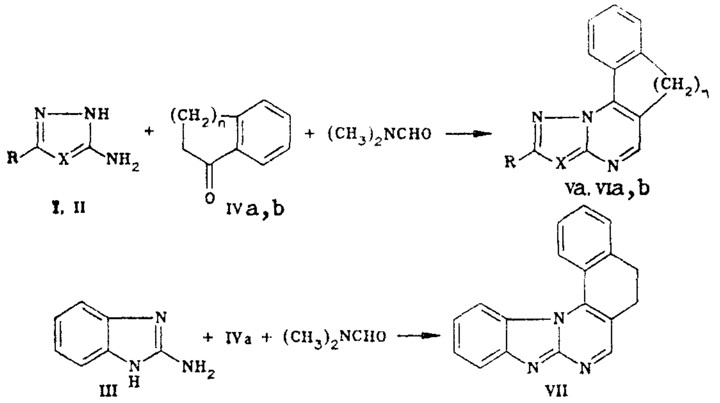
We have established that refluxing solutions of amines I-III and tetralone (IVa) in DMF (for 7 h) leads to pyrazolo- and 1,2,4-triazolo[1,5-*a*]pyrimidine derivatives Va and VIa and pyrimido[1,2-*a*]benzimidazole derivative VII. Derivative VIb was similarly obtained from 3,5-diamino-1,2,4-triazole (II) and benzosuberone (IVb).

Compounds V-VII (see Table 1) were identified as azolopyrimidine derivatives on the basis of the following data. The mass spectra of Va, VIa, and VII (m/z 235, 237, and 271, respectively, for the molecular ions) indicate that their molecular masses are 5 units smaller than the sums of the molecular masses of the corresponding amines and ketones. This is possible only if in the condensation, in addition to splitting out of water, a —CH= group, for which DMF acts as the synthone, is introduced. Signals of aromatic and heteroaromatic protons and protons of $(CH_2)_n$ groups appear in the PMR spectra of V-VII; a singlet of the proton of a —CH= group stands out distinctly in the weak-field region. The signals of the ortho proton of a benzene ring are also shifted to the region of high δ values in the spectra of Va, VIa, and VII, while in the spectrum of VIb they are overlapped by the signals of the remaining aromatic protons. In our opinion, this fact should be associated with the more planar (as compared with VIb) structures of the Va, VIa, and VII molecules.



I, V X=CH, R=CH_3; II, VI X=N, R=NH_2; IV—VI a $n=2$, b $n=3$

The electronic spectra of V-VII are similar to the spectra of the corresponding azolopyrimidine systems [1, 2]. The difference in the three-dimensional structures of VIa, b is reflected in the longer-wave and more intense absorption of a solution of VIa as compared with its homolog VIb. Let us also note the bathochromic shift and the increase in the intensity of the long-wave absorption band on passing to VII from 4-phenylpyrimido[1,2-*a*]benzimidazole (λ_{max}

TABLE 1. Characteristics of Va-VII

Compound	mp, °C	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	δ, ppm (J, Hz), in CF_3COOH	Yield, %
Va	200	331 (12,2)	8,89 (1H, s, CH); 8,43 (1H, d, J=7,7, ArH); 7,4...7,5 (3H, m, ArH); 6,46 (1H, s, CH); 2,8...3,0 (4H, m, $(CH_2)_2$)	48
VIa	275	359 (17,1)	8,82 (1H, s, CH); 8,43 (1H, d, J=7,6, ArH); 7,4...7,8 (3H, m, ArH); 3,1...3,2 (4H, m, $(CH_2)_2$)	51
VIb	277	341 (12,1)	8,95 (1H, s, CH); 7,5...7,8 (4H, m, ArH); 2,4...2,9 (6H, m, $(CH_2)_3$)	46
VII	299	355 (24,2)	9,42 (1H, s, CH); 8,39 (1H, d, J=7,9, ArH); 7,3...8,3 (7H, m, ArH); 3,0...3,1 (4H, m, $(CH_2)_2$)	53

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320 nm, ε $5.5 \cdot 10^3$ [2]). This fact becomes understandable if one considers that, according to the data in [2], the phenyl substituent in 4-phenylpyrimido[1,2-*a*]benzimidazoles is virtually perpendicular to the plane of the heteroring, while this sort of orientation is impossible in VII because of the presence of an annelated six-membered carbocycle.

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SYNTHESIS OF ARYL 4(5)-IMIDAZOLYL KETONES

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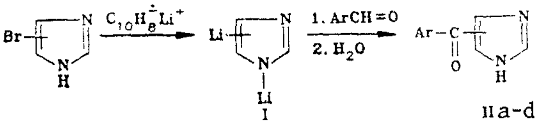
It is known that arylhetarylcarbinols are formed in the reaction of active organometallic compounds of N-substituted azoles (with N-alkyl, N-aralkyl, and N-aryl substituents) with aromatic aldehydes [1, 2]. However, instead of the expected aryl[4(5)-imidazolyl]carbinols, we obtained aryl 4(5)-imidazolyl ketones IIa-d by the action of aromatic aldehydes on imidazolyl-1,4(5)-dilithium, formed from 4(5)-bromoimidazole and naphthyllithium.



II a $Ar=C_6H_5$, b $Ar=2\text{-}CH_3OC_6H_4$, c $Ar=4\text{-}CH_3OC_6H_4$, d $Ar=3,4\text{-}(CH_3O)_2C_6H_3$

This pathway for obtaining ketones II gives better results than the synthesis of the ketones by the known reaction of organolithium compounds with carboxylic acid nitriles.

A solution of 1.1 g (7.5 mmole) of 4(5)-bromoimidazole in 10 ml of THF was added in the course of 5 min with stirring in an argon atmosphere at −10°C to −15°C to naphthyllithium obtained from 0.21 g (30 mmole) of finely ground lithium and 3.84 g (30 mmole) of naphthalene in 20 ml of THF, 5 min after which a solution of 35 mmole of the aromatic aldehyde in 10 ml of THF was added, and the mixture was maintained at −10°C to −15°C for 30 min and at 20-25°C for 2 h. The usual workup gave aryl 4(5)-imidazolyl ketones IIa-d in 48-63% yields.

Ketones IIa and IIc are formed in 17% and 24% yields, respectively, when the aromatic aldehydes are replaced by benzonitrile and p-methoxybenzonitrile.

Phenyl 4(5)-Imidazolyl Ketone (IIa). This compound had mp 149-150°C (from aqueous alcohol). IR spectrum ($CHCl_3$): 1640 (C=O), 3440 cm^{-1} (NH). PMR spectrum (CF_3COOH): 7.25 (5H, m, C_6H_5): 7.70 [1H, s, 4(5)-H], 8.54 ppm (1H, m, 2-H). The yield was 55%.

2-Methoxyphenyl 4(5)-Imidazolyl Ketone (IIb). This compound had mp 129-130°C (from ethyl acetate). IR spectrum ($CHCl_3$): 1642 (C=O), 3448 cm^{-1} (NH). PMR spectrum (CF_3COOH): 3.38 (3H, s, OCH_3), 6.87 (4H, m, C_6H_4), 7.50 [1H, s, 4(5)-H], 8.42 ppm (1H, m, 2-H). The yield was 52%.

4-Methoxyphenyl 4(5)-Imidazolyl Ketone (IIc). This compound had mp 191-192°C (from alcohol). IR spectrum ($CHCl_3$): 1633 (C=O), 3438 cm^{-1} (NH). PMR spectrum (CF_3COOH): 3.52 (3H, s, OCH_3), 6.71 (2H, d, J = 9.45 Hz, C_6H_4), 7.58 (2H, d, J = 9.45 Hz, C_6H_4), 7.72 [1H, s, 4(5)-H], 8.57 ppm (1H, m, 2-H). The yield was 48%.

3,4-Dimethoxyphenyl 4(5)-Imidazolyl Ketone (IId). This compound had mp 208-209°C (from alcohol). IR spectrum ($CHCl_3$): 1630 (C=O), 3432 cm^{-1} (NH). PMR spectrum (CF_3COOH): 3.57 (6H, s, two OCH_3 groups), 6.70 (1H, d, J = 9.45 Hz, C_6H_3), 7.20 (1H, s, C_6H_3), 7.33 (1H, d, J = 9.45 Hz, C_6H_3), 7.75 [1H, s, 4(5)-H], 8.57 ppm (1H, m, 2-H). The yield was 63%.

The results of elementary analysis of ketones IIa-d were in agreement with the calculated values.

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