SYNTHESIS OF DERIVATIVES OF 5-AMINO-4-ACYL-1,2,3-TRIAZOLE, 8-AZAPURINE, AND 1,2,3-TRIAZOLO[4,5-b]PYRIDIN-7-ONE USING N,N-ACETALS OF ACYLKETENES AND TOSYLAZIDE

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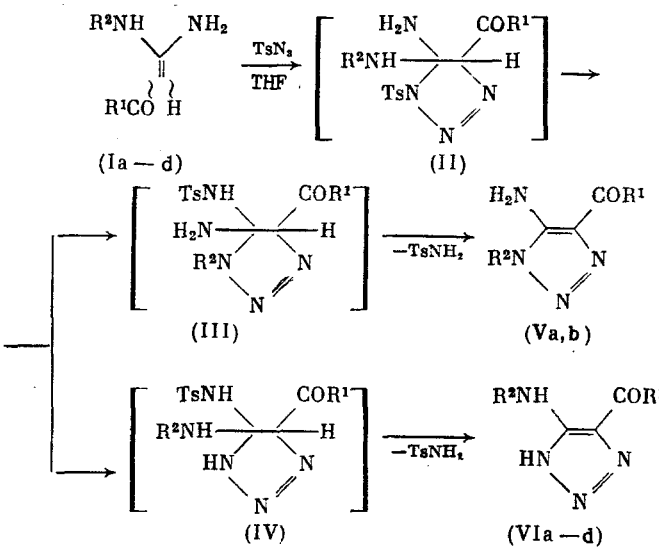
By reaction of N,N-acetals of acylketenes with tosylazide there were synthesized 5-amino-4-acyl-1,2,3-triazoles substituted at the endo(N^1)- or exocyclic nitrogen atom. Triazoles containing a free NH_2 group were used in the synthesis of the corresponding 8-azapurines and 4-acetyl-5-benzoylamino-1,2,3-triazole afforded 2-methyl-2H,4H-1,2,3-triazolo[4,5-b]pyridin-7-one.

A growing interest in N,N-acetals of ketenes is caused by the possibility of their application as reagents for creating heterocyclic systems (see [1, 2] and literature cited therein). Recently we proposed a convenient new method of synthesizing N,N-acetals of acylketenes (AAKs), which includes $Ni(acac)_2$ catalyzed addition of β-diketones or esters of β-keto acids to cyanamides with formation of N,N-acetals of diacylketenes and deacylation of the latter with MeOH in the presence of Co^{2+} acetate [3]. The AAKs obtained this way contain an unsubstituted amino group, which substantially increases their synthetic potential. In particular, the possibility was demonstrated of their application as 1,3-dinucleophiles for annealation of a pyrrole ring to give derivatives of 1,2,4-triazine and quinoxaline [4].

This paper reports the use of AAKs in the synthesis of derivatives of 5-amino-1,2,3-triazole, 1,2,3-triazolo[4,5-d]pyrimidine (8-azapurine), and 1,2,3-triazolo[4,5-b]pyridin-7-one.



(1)

$R^1 = Me$, $R^2 = Ph$ (a); $R^1 = R^2 = Ph$ (b); $R^1 = Me$, R^2 = 4,6-dimethylpyrimidin-2-yl (c); $R^1 = Me$, $R^2 = PhCO$ (d).

Recently a number of papers appeared which deal with conversions of functionalized enamines with azides [5-7]. It was shown particularly that AAKs obtained by acylation of 1,1-dimorpholinoethylene react with p-nitrophenyl azide forming 4-acyl-5-morpholino-1-(p-nitrophenyl)-1,2,3-triazoles [6]. Quite recently a report was published on the synthesis of 4-acyl-5-tosylamino-1,2,3-triazoles by the action of tosyl azide (TsN_3) on S,N-acetals of acylketenes in the presence of alkali [7].

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published on the synthesis of 4-acyl-5-tosylamino-1,2,3-triazoles by the action of tosyl azide (TsN_3) on S,N-acetals of acylketenes in the presence of alkali [7].

We have found that reaction of AAKs (Ia-c) with TsN_3 proceeds easily in THF at 20°C in the absence of alkaline catalysts with formation of substituted 5-amino-4-acyl-1,2,3-triazoles (V) or (VI). Reactions of TsN_3 with (Id) proceeds upon boiling in THF.

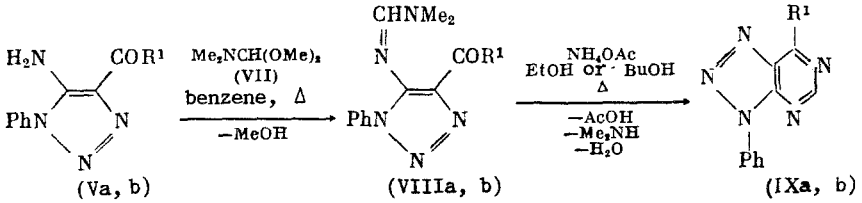
Apparently process (1) is accompanied by rearrangement (of the Dimroth type) of the initial cycloadduct (II) and leads to (V, VI) by elimination of $TsNH_2$ in intermediates (III) and (IV). For (Ic, d) reaction proceeds regiospecifically with formation of (VIc, d) which contain substituent R^2 at the exocyclic N atom. Yields of (VIc, d) are 94 and 70%, respectively. In the reaction of (Ia, b) with TsN_3 there were obtained (VIa, b) as well as isomers (Va, b) which have a free NH_2 group. Products can be separated by column chromatography. Yields of compounds (Va) and (Vb) are 73 and 53% and of (VIa) and (VIb) 13 and 33%, respectively.

The structures of (V) and (VI) were confirmed by spectral data (IR, ^1H and ^{13}C NMR spectroscopy, mass spectrometry). Compounds (Vb) and (VIb) are identical with the ones obtained from 4-benzoyl-5-tosylamino-1-phenyl-1,2,3-triazoles [7].

In the mass spectra the relative intensities of $[M]^{+\cdot}$ peaks for (VIa, b) are substantially higher than in the spectra of isomeric (Va, b). PMR spectra of (V) have one singlet for the NH_2 group at δ 6.0-5.7 ppm, while spectra of compounds (VI) contain two NH signals at δ ~ 9 and ~15-14 ppm.

It is known that derivatives of 1,2,3-triazole containing an unsubstituted amino group are convenient starting compounds for synthesis of 1,2,3-triazolo[4,5-d]pyrimidines (8-azapurines) — compounds with a wide range of biological activity, particularly anti-tumor [8, 9]. Thus, 5-amino-1-benzyl-4-formyl-1,2,3-triazole is converted into the corresponding 8-azpurines by the action of orthoesters or Vilsmeier reagent followed by treatment of the condensation products with ammonium acetate or alcoholic NH_3 solution [10].

To obtain 8-azapurines from (Va, b) we have used the dimethylacetal of dimethylformamide (VII). Boiling of a solution of the above reagents in benzene leads to 4-acyl-5-[(dimethylamino)methylene]amino-1-phenyl-1,2,3-triazole (VIIIa, b) with high yield, which upon heating with ammonium acetate in EtOH or BuOH undergoes cyclization to substituted 8-azapurines (IXa, b)

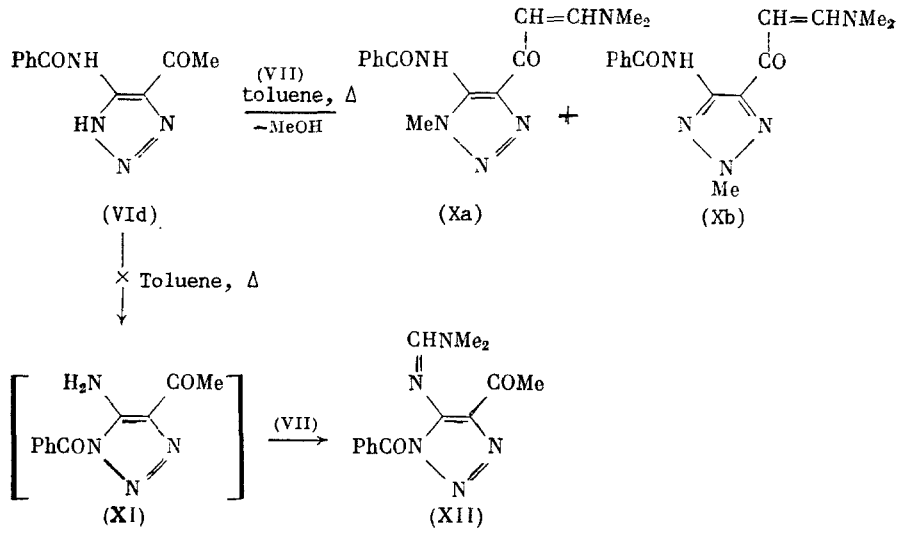


$R^1 = Me$ (a), $R^1 = Ph$ (b). (2)

Compounds (IX) can be synthesized also by the scheme (I) → (V) → (VIII) → (IX) without formation of intermediate (V). Thus, from (Ib) there was obtained (IXb) with 30% yield per starting AAK. The structures of compounds (IX) were confirmed by spectral methods (see Experimental). Intermediates (VIII) were characterized by PMR spectra.

Synthesis of (IXa, b) from AAKs is a fully acceptable alternative to the previously described method of obtaining these compounds based on the use of relatively inaccessible 3-phenyl-7-chloro-3H-1,2,3-triazolo[4,5-d]pyrimidine [11, 12].

Reaction of 4-acetyl-5-benzoylamino-1,2,3-triazole (VId) with (VII) upon boiling in toluene proceeds anomalously. There is not observed under these conditions the 1,3(N → N)-migration of the benzoyl group to (VId) with formation of 1,2,3-triazole (XI) containing an unsubstituted amino group and further conversion of (XI) into amidine (XII). It turned out that in the condensation with (VII) a methyl group of (VId) participates. Methylation of the triazole ring with the excess (VII) proceeds simultaneously. As a result a mixture was obtained of isomeric compounds (Xa) and (Xb) which were separated by column chromatography (yields 38 and 51%, respectively).



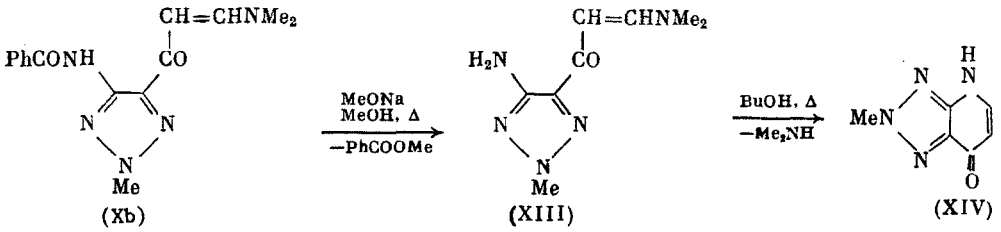
(3)

The structures of (Xa, b) were confirmed by spectral data. The position of the Me group in the triazole ring was established unambiguously on the basis of ^{13}C and ^{15}N NMR (INEPT) spectra. In the ^{13}C NMR spectrum of (Xb) the C^5 signal is upfield (δ 146.32 ppm) compared to the corresponding signal for (Xa) (δ 137.42 ppm; see [13]: transition from 1,2,3-triazole derivatives substituted at N^1 to those substituted at N^2 is accompanied by a downfield shift of the C^5 signal). For (Xa) the C^5 signal is a quartet ($^3J_{C^5,Me}$ = 2.2 Hz) while in (Xb) coupling between atoms C^4 and C^5 and the Me group is absent. The ^{15}N NMR spectrum of (Xa) in $CDCl_3$ (35°C) contains signals of two N atoms coupled with the Me group (q. N^1 at δ −152.69 ppm, $^2J_{N^1,Me}$ = 2.0 Hz and N^2 at δ −28.74 ppm, $^3J_{N^2,Me}$ = 1.8 Hz) and for (Xb) this interaction exists for all endocyclic N atoms (q. N^2 at δ −146.46 ppm, $^2J_{N^2,Me}$ = 2.5 Hz, N^1 at δ −74.55 ppm, $^3J_{N^1,Me}$ = 2.5 Hz and N^3 at δ −52.43 ppm, $^3J_{N^3,Me}$ = 2.0 Hz).

Compound (Xb) is easily debenzoylated upon boiling with MeONa in MeOH with formation of 5-amino-4-[3-(dimethylamino)acryloyl]-2-methyl-1,2,3-triazole (XIII) which in boiling BuOH is cyclized to 2-methyl-2H,4H-1,2,3-triazolo[4,5-b]pyridin-7-one (XIV) [yield 60% per (Xb)].

The mass spectrum of (XIV) contains a high intensity molecular ion peak. In the IR spectrum of this compound in KBr the CO absorption band is observed at 1635 cm^{-1}.

The examples shown indicate that reaction of AAKs with TsN_3, which leads to formation of a 1,2,3-triazole ring, can be also used for obtaining condensated 1,2,3-triazoles.



(4)

EXPERIMENTAL

The PMR spectra were recorded on a Bruker WM-250 instrument and ^{13}C and ^{15}N NMR spectra on a Bruker AM-300 instrument. The ^{15}N chemical shifts were measured relative to $MeNO_2$ (external standard). IR spectra were recorded on a UR-20 instrument. Mass spectra were obtained on a Varian MAT CH-6 spectrometer.

Analytical TLC was performed on Kieselgel 60 F_{254} plates (Merck) for (Va, b) and (VIa, b, d) or Silufol UV-254 (for the remaining compounds). The following eluents were used (shown in brackets after R_f): $CHCl_3$–EtOH 40:1 (1), $CHCl_3$ (2), benzene–EtOH 20:1 (3), benzene–EtOH 50:1 (4), $CHCl_3$–EtOH 20:1 (5), and $CHCl_3$–EtOH 10:1 (6). Preparative chromatography was carried out on columns with SiO_2, L 40/100 μm.

Starting compounds (Ia-d) were synthesized according to [3] and TsN_3 according to [14].

Reaction of N,N-Acetates of Acylketenes (Ia-d) with TsN_3 (general method). A mixture of 2 mmoles of (Ia-c) and 2.5 mmoles of TsN_3 in 8 ml of THF was stirred for 3 h at 20°C [for (Ia, b)] or 8 h [for (Ic)]. In the case of (Id) the mixture was boiled for 8 h. In reactions with (Ia, b) solvent was distilled off, the residue was chromatographed on a column (eluent $CHCl_3$), and (Va, b) and (VIa, b) were obtained. For (Ic, d) the mixture was left at 20°C overnight, then the precipitated crystals were filtered and (VIc, d) were obtained [in the synthesis of (VId) an additional amount of product was obtained by column chromatography of the residue after evaporation of filtrate].

5-Amino-4-acetyl-1-phenyl-1,2,3-triazole (Va) was obtained in the amount of 0.295 g (73%), mp 120-121°C (benzene–hexane, 1:1), R_f 0.51 (1). Mass spectrum, m/z (%): 202(35) $[M]^+$, 159(19) $[M-COMe]^+$, 132(58) $[M-N_2-CH_2=C=O]^+$, 131(46) $[M-N_2-COMe]^+$, 43(100) $[COMe]^+$. Found, %: C 59.45; H 4.75; N 27.66. $C_{10}H_{10}N_4O$. Calculated, %: C 59.40; H 4.98; N 27.71. IR spectrum in $CHCl_3$ (ν, cm^{-1}): 3490, 3375 (NH_2), 1660 (CO), 1620, 1600, 1530 (multiple bonds). PMR spectrum in $CDCl_3$ (δ, ppm): 7.62-7.47 m (Ph), 5.70 br. s (NH_2), 2.68 s (Me). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 193.75 (CO), 144.48 (C^5), 129.12 (C^4), 134.26, 130.09, 129.64, 123.91 (Ph), 26.19 (Me).

4-Acetyl-5-phenylamino-1,2,3-triazole (VIa) was obtained in the amount of 0.053 g (13%), mp 127-128°C (benzene–hexane, 1:1), R_f 0.46 (1). Mass spectrum, m/z (%): 202(80) $[M]^+$, 159(10) $[M-COMe]^+$, 132(15) $[M-N_2-CH_2=C=O]^+$, 131(10) $[M-N_2-COMe]^+$, 43(100) $[COMe]^+$. Found, %: C 59.37; H 4.74; N 28.13. $C_{10}H_{10}N_4O$. Calculated, %: C 59.40; H 4.98; N 27.71. IR spectrum in $CHCl_3$ (ν, cm^{-1}): 3440, 3375 (NH), 1665 (CO), 1600, 1575 (multiple bonds). PMR spectrum in DMSO-d_6 (δ, ppm): 15.00 br. s (NH), 8.51 br. s (NH), 7.56 d (2H Ph), 7.30 t (2H Ph), 6.94 t (1H Ph), 2.55 s (Me). ^{13}C NMR spectrum in MeOH-d_4 (δ, ppm): 196.13 (CO), 150.75 (C^5), 131.97 (C^4), 141.89, 130.16, 122.61, 118.38 (Ph), 26.58 (Me).

5-Amino-4-benzoyl-1-phenyl-1,2,3-triazole (Vb). There was obtained 0.280 g (53%) of the compound, mp 140-141°C (benzene–hexane, 1:2); 140-141°C [7], R_f 0.32 (2). ^{13}C NMR spectrum in CD_2Cl_2 (δ, ppm): 186.56 (CO), 147.42 (C^5), 129.34 (C^4), 137.72, 134.74, 132.80, 130.53, 130.44, 130.06, 128.52, 124.45 (2 Ph).

4-Benzoyl-5-phenylamino-1,2,3-triazole (VIb) was obtained in the amount of 0.174 g (33%), mp 160-161°C (benzene–hexane, 1:1); 160-161°C [7], R_f 0.25 (2). PMR spectrum in DMSO-d_6 (δ, ppm): 15.20 br. s (NH), 9.02 br. s (NH), 8.30 d (2H Ph), 7.82-7.45 m (5H phenyl), 7.32 t (2H Ph), 7.00 t (1H Ph).

4-Acetyl-5-(4,6-dimethylpyrimidin-2-yl)amino-1,2,3-triazole (VIc) was obtained in the amount of 0.436 g (94%), mp 249-251°C (benzene–hexane, 3.5:1), R_f 0.24 (1). Mass spectrum, m/z (%): 232 (73) $[M]^{+\cdot}$; 204 (42) $[M-N_2]^+$, 203 (60) $[M-N_2-H]^+$, 189 (34) $[M-MeCO]^+$, 187 (66) $[M-3Me]^+$, 108 (78) $[C_6H_8N_2]^+$, 107 (100) $[C_6H_7N_2]^+$. Found, %: C 51.81; H 5.29; N 35.82. $C_{10}H_{12}N_6O$. Calculated, %: C 51.71; H 5.21; N 36.19. IR spectrum in $CHCl_3$ (ν, cm^{-1}): 3360 (NH), 3300-3000 (NH, CH), 1665 (CO), 1620, 1600, 1555 (multiple bonds). PMR spectrum in $CDCl_3$ (δ, ppm): 14.00 br. s (NH), 9.48 br. s (NH), 6.75 s (CH=), 2.72 s (MeCO), 2.49 s (2 Me). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 194.35 (CO), 157.54 (C^4 and C^6 pyrim.), 140.19 (C^2 pyrim.), 130.22 (C^5 triaz.), 127.09 (C^4 triaz.), 114.50 (C^5 pyrim.), 26.56 (MeCO), 24.03 (2 Me).

4-Acetyl-5-benzoylamino-1,2,3-triazole (VId) was obtained in the amount of 0.322 g (70%), mp 261-263°C (toluene). Mass spectrum, m/z (%): 230 (100) $[M]^{+\cdot}$, 202 (36) $[M-N_2]^+$, 201 (32) $[M-N_2-H]^+$, 174 (25) $[M-N_2-CO]^+$. Found, %: C 57.39; H 4.23; N 24.52. $C_{11}H_{10}N_4O_2$. Calculated, %: C 57.38; H 4.38; N 24.34. IR spectrum in KBr (ν, cm^{-1}): 3344, 3168 (NH), 1676, 1636 (CO), 1588, 1528 (multiple bonds). PMR spectrum in DMSO-d_6 (δ, ppm): 15.70 br. s (NH), 10.62 br. s (NH), 7.96 d (2H Ph), 7.70-7.45 m (3H, Ph), 2.54 s (Me). ^{13}C NMR spectrum in DMSO-d_6 (δ, ppm): 192.94 (CO), 164.77 (NCO), 139.52 (C^5), 134.25 (C^4), 132.70, 132.40, 128.85, 127.63 (Ph), 27.12 (Me).

7-Methyl-3-phenyl-3H-1,2,3-triazolo[4,5-d]pyrimidine (IXa). A mixture of 0.101 g (0.5 mmole) of (Va) and 0.276 ml (2 mmoles) of (VII) in 5 ml of benzene was boiled under Ar for 1 h. Solvent was distilled off and there was obtained 0.125 g (97%) of (VIIIa), R_f 0.27 (3). PMR spectrum in $CDCl_3$ (δ, ppm): 8.85 s (CH=), 7.78 d (2H Ph), 7.47 t (2H Ph), 7.38 t (1H Ph), 3.12 s and 2.98 s (NMe_2). 0.770 g (10 mmoles) of NH_4OAc in 3 ml of EtOH was added to (VIIIa) and the mixture was boiled for 6 h. Solvent was distilled off and the residue extracted (2 × 20 ml) with benzene. Benzene was removed under vacuum, the residue was sublimed at 85-90°C (1 mm) to give 0.071 g (67%) of (IXa), mp 119-120°C, 116-117°C [11], R_f 0.37 (3).

Mass spectrum, m/z (%): 211 (18) $[M]^{+\cdot}$, 183 (74) $[M-N_2]^+$, 142 (100) $[M-N_2-MeCN]^+$. IR spectrum in $CHCl_3$ (ν, cm^{-1}): 1600, 1575, 1510 (multiple bonds). PMR spectrum in $CDCl_3$ (δ, ppm): 9.08 s (CH=), 8.23 d (2H Ph), 7.60 t (2H Ph), 7.47 t (1H Ph), 3.08 s (Me). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm; J, Hz): 163.58 (C^7, $^2J_{C^7,Me}$ = 6.7, $^3J_{C^7,H^5}$ = 10.0), 156.36 (C^5, $^1J_{C^5,H}$ = 206.0), 148.03 (C^{3a}, $^3J_{C^{3a},H^5}$ = 2.4), 136.34 (C^{7a}, $^3J_{C^{7a},Me}$ = 2.9, $^4J_{C^{7a},H^5}$ = 2.2), 135.94, 129.73, 128.78, 121.35 (Ph), 20.47 (Me, $^1J_{C,H}$ = 129.0).

3,7-Diphenyl-3H-1,2,3-triazolo[4,5-d]pyrimidine (IXb). a) Synthesis from (Vb). As in synthesis of (IXa), from 0.132 g (0.5 mmole) of (Vb) and 0.270 ml (2 mmoles) of (VII) there was obtained 0.140 g (90%) of (VIIIb) (purified by column chromatography, eluent benzene), R_f 0.21 (4). PMR spectrum in $CDCl_3$ (δ, ppm): 8.73 s (CH=), 8.18 d (2H Ph), 7.85 d (2H Ph), 7.61-7.37 m (6H Ph), 3.13 s and 3.02 s (NMe_2). To (VIIIb) there was added 0.770 g (10 mmoles) of NH_4OAc in 3 ml BuOH and the mixture was boiled for 8 h. Solvent was distilled off and the residue was extracted (2 × 20 ml) with benzene. Benzene was removed under vacuum and the residue was chromatographed on a column (eluent benzene). There was obtained 0.070 g (52%) of (IXb), mp 130-131°C (hexane), 127-128°C [11], R_f 0.65 (4). Mass spectrum, m/z (%): 273 (60) $[M]^{+\cdot}$; 245 (100) $[M-N_2]^+$, 244 (78) $[M-N_2-H]^+$, 142 (86) $[M-N_2-PhCN]^+$. IR spectrum in $CHCl_3$ (ν, cm^{-1}): 1590, 1560, 1510 (multiple bonds). PMR spectrum in $CDCl_3$ (δ, ppm): 9.23 s (CH=), 8.99 d (2H Ph), 8.27 d (2H Ph), 7.72-7.58 m (5H Ph), 7.50 t (1H Ph). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm; J, Hz): 158.36 (C^7, $^3J_{C^7,H^5}$ = 10.0, $^3J_{C^7,o\text{-}H,Ph}$ = 4.2), 156.45 (C^5, $^1J_{C^5,H}$ = 206.0), 149.66 (C^{3a}, $^3J_{C^{3a}H^5}$ = 12.1), 134.05 (C^{7a}), 135.93, 134.26, 132.78, 130.43, 129.67, 129.03, 128.76, 121.56 (2Ph).

b) Synthesis from (Ib). From a reaction mixture, obtained as in the synthesis of (Vb) from 0.600 g (2.5 mmoles) of (Ib) and 0.600 g (3.0 mmoles) of TsN_3, solvent was removed and the mixture was boiled with 2.0 ml (15.0 mmoles) of (VII) in 20 ml of benzene under Ar for 4 h. Solvent was distilled off and the residue chromatographed on a column (eluent benzene) to give 0.480 g [60% per (Ib)] of (VIIIb), from which, as described above, 0.210 g of (IXb) [30% per (Ib)] was obtained.

5-Benzoylamino-4-[3-(dimethylamino)acryloyl]-1-methyl-1,2,3-triazole (Xa) and 5-benzoylamino-4-[3-(dimethylamino)acryloyl]-2-methyl-1,2,3-triazole (Xb). A mixture of 0.180 g (0.78 mmole) of (VId) with 0.3 ml (2.26 mmoles) of (VII) was boiled in 5 ml of toluene under Ar for 2 h. Solvent was distilled off and the residue was chromatographed on a column (eluent $CHCl_3$). There was obtained 0.090 g (38%) of (Xa) and 0.120 g (51%) of (Xb). Compound (Xa); mp 189-190°C (benzene–hexane, 1:1), R_f 0.35 (5). Mass spectrum, m/z (%): 299 (100) $[M]^{+\cdot}$, 282 (24) $[M-Me-2H]^+$, 227 (24) $[M-N_2-Me_2N]^+$, 105 (100) $[PhCO]^+$. Found, %: C 60.54; H 5.79; N 23.60. $C_{15}H_{17}N_5O_2$. Calculated, %: C 60.19; H 5.72; N 23.40. IR spectrum in $CHCl_3$ (ν, cm^{-1}): 3400-3150 (NH), 1700, 1645 (CO), 1590, 1520 (C=N and C=C). PMR spectrum in $CDCl_3$ (δ, ppm): 10.84 br. s (NH), 8.02 d (2H Ph), 7.85 br. s (NCH=), 7.60 t (1H, Ph), 7.51 t (2H Ph), 6.11 br. s (COCH=), 4.18 s (NMe), 3.14 s and 2.94 s (NMe_2). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm; J, Hz): 182.75 (CO), 165.48 (NCO), 137.42 (C^5, $^3J_{C^5,Me}$ = 2.2), 134.75 (C^4), 132.90, 132.45, 128.93, 127.88 (Ph), 153.80 (NCH=), 92.50 (COCH=), 37.87 (NMe), 45.19 and 37.42 (NMe_2). Compound (Xb): mp 232-233°C (benzene), R_f 0.44 (5). Mass spectrum, m/z (%): 299 (41) $[M]^{+\cdot}$, 282 (23) $[M-Me-2H]^+$, 255 (11) $[M-Me_2N]^+$, 222 (8) $[M-Ph]^+$, 194 (15) $[M-COPh]^+$, 105 (100) $[PhCO]^+$. Found %: C 60.40; H 5.73; N 23.47. $C_{15}H_{17}N_5O_2$. Calculated, %: C 60.19; H 5.72; N 23.40. IR spectrum in $CHCl_3$ (ν, cm^{-1}): 3310 (NH), 1690, 1645 (CO), 1555, 1510 (C=N and C=C). PMR spectrum in $CDCl_3$ (δ, ppm; J, Hz): 11.21 br. s (NH), 8.20 d (2H Ph), 7.84 d (NCH=, ^3J = 12.8), 7.59-7.43 m (3H Ph), 5.86 d (COCH=, ^3J = 12.8), 4.21 s (NMe), 3.15 s and 2.94 s (NMe_2). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 182.40 (CO), 163.51 (NCO), 146.30 (C^5), 133.45 (C^4), 133.62, 132.06, 128.70, 127.50 (Ph), 153.80 (NCH=), 91.93 (COCH=), 42.42 (NMe), 45.20 and 37.41 (NMe_2).

2-Methyl-2H,4H-1,2,3-triazolo[4,5-b]pyridin-7-one (XIV). A solution of 0.120 g (0.40 mmole) of (Xb) and 0.086 g (1.6 mmoles) of MeONa in 4 ml of MeOH was boiled under Ar for 12 h. After cooling 0.1 ml of AcOH was added, solvent was distilled off, and the residue chromatographed on a column (eluent $CHCl_3$). There was obtained 0.065 g (83%) of (XIII), R_f 0.42 (6). Mass spectrum, m/z: 195 $[M]^{+\cdot}$. PMR spectrum in $CDCl_3$ (δ, ppm): 7.75 d (NCH=), 5.82 d (COCH=), 5.05 br. s (NH_2), 4.00 s (NMe), 3.12 s and 2.90 s (NMe_2). Compound (XIII) was boiled in 4 ml of BuOH for 4 h and cooled to ~20°C. The precipitate was filtered and 0.020 g of (XIV) was obtained. (From filtrate after evaporation and washing the residue with 1.5 ml of $CHCl_3$ an additional 0.016 g was obtained.) Total yield was 60% per (Xb), mp 276-278°C

(BuOH), R_f 0.10 (6). Found, %: C 47.96; H 4.09; N 36.87. $C_6H_6N_4O$. Calculated, %: C 48.00; H 4.03; N 37.32. Mass spectrum, m/z: 150 $[M]^+$, IR spectrum in KBr (ν, cm^{-1}): 3200-2400 (NH, CH), 1635 (CO), 1620, 1597, 1570 (C=N, C=C). PMR spectrum in DMSO-d_6 (δ, ppm; J, Hz): 12.25 br. s (NH), 7.83 d (H^5, ^3J = 5.8), 5.95 d (H^6, ^3J = 5.8), 4.32 s (Me).

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OXIDATIVE DIMERIZATION OF HETEROCYCLIC NITRONES, DERIVATIVES OF PYRROLINE AND IMIDAZOLINE

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The oxidation of β-oxonitrones, derivatives of pyrroline and imidazoline, afforded symmetric dimers with a C–C bond and dehydrodimers with a C=C bond. Oxidation of the trifluoroacetyl imidazoline derivative afforded an asymmetric dimer. The oxidative dimerization of endocyclic β-oxonitrones, derivatives of pyrroline, proceeded much faster than that of exocyclic β-oxonitrones, derivatives of imidazoline. Imidazoline derivatives containing a perfluorophenyl or cyano group at the α-carbon atom on the nitrone group also underwent oxidative dimerization.

Oxidative dimerization, with formation of a carbon–carbon saturated bond or an ethylene bond [1, 2], is a characteristic reaction of alkyl nitrones (I) conttaining an electron-acceptor substituent in the β-position. Vinyl nitroxyl radical (II) is formed during the first stage of the reaction [3, 4]. Radicals (II), in which the spin density is distributed between nitroxyl and vinyl fragments [5], are relatively stable and may be observed by means of EPR [6]. In some cases the less stable C–O dimer (V) is formed [7] (see top of following page).

In continuing the study of heterocyclic nitrones, derivatives of pyrroline [8] and imidazoline [9], we examined their oxidative reactions in order to elucidate the characteristics of these reactions in a series of heterocyclic nitrones.

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