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SYNTHESIS AND NMR SPECTROSCOPIC STUDY OF DERIVATIVES OF PYRAZOLO[1,5-*a*]PYRIMIDINES

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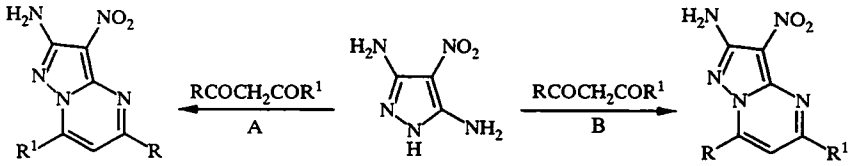
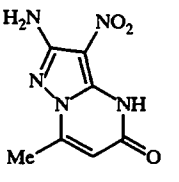
Reactions of 3,5-diamino-4-nitropyrazole with asymmetric β-dicarbonyl compounds formed pyrazolo[1,5-a]pyrimidines, which in turn were used as the starting compounds in the reaction with dimethylformamide diethylacetal. The structure of the compounds obtained was studied by NMR spectroscopy in experiments involving the homonuclear Overhauser effect.

Using push-pull enamines, we have recently devised a new approach to the synthesis of 3,5-diamino-4-nitropyrazole (I) [1] and established that in the presence of methanolic HCl (0.1 mole per mole of compound I), this compound tends to react with β-diketones to form derivatives of pyrazolo[1,5-*a*]pyrimidines [2]. Moreover, in [2], the starting compounds chosen were symmetric β-diketones; this precluded the possibility of reactions in alternative directions and made it possible to get a better idea of the structure of the bicyclic compounds obtained. The present paper investigates the reactions of pyrazole I with asymmetric β-dicarbonyl compounds; this caused an uncertainty in the occurrence of the process and made it necessary to study in detail the pyrazolopyrimidines obtained. Indeed, the direction (A or B) in which the initial step will take place is not obvious, and accordingly, a special proof of the structure of the heterocycles being formed is necessary.



The first stage of the study concerned the reaction of diaminonitropyrazole I with acetoacetic ester. Heating of these compounds in the presence of HCl/MeOH readily caused formation in high yield of pyrazolopyrimidine II for which, depending on which of the groups (CO-ketone or COOEt) reacts with the first, two structures are possible (IIA and IIB). The enamine derivative III is formed as an intermediate which, as is generally characteristic of enamines [3], readily hydrolyzes to IIA.

IIA



IIB

It should be noted that chemically, structure IIA is more probable, since it can reasonably be postulated that in acid medium, the initial step of the reaction will involve a primary amino group, not the NH group of the pyrazole ring (pK_a of I (proton detachment) is 8.48 [2], i.e., under these conditions, formation of an anion is impossible), and the reaction of acetoacetic ester with amines usually involves formation of enamines, not amides (see for example [4]). However, the presence

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TABLE 1. Data of ^1H NMR Spectra for Compounds II-XV, δ, ppm, SSCC (J, Hz), OE (all spectra were obtained with DMSO-D_6 used as the solvent and a temperature of +23°C)

Compound	6-CH	2-NH_2, NH	4-NH (S)	5-C-CH_3 5-C-Ph	7-C-OCH_2CH_3 C(O)OCH_2CH_3 7-C-Ph	N=CH	$N(CH_3)_2$ (3H, s, CH_3)	Overhauser effect		
								irradiated signal	response signal	%
1	2	3	4	5	6	7	8	9	10	11
IIA	5,94 (s)	6,67 (s)	12,37	2,36 (s)				5-CH_3	6-CH	19
								6-CH	5-CH_3	3
								NH	5-CH_2	4
III	6,02 (s)	11,80 (nar.s)	12,55 (highly br.s)	2,39 (s) 2,47 (3H, s, CH_3-side chain)	1,22 (3H, t , CH_3), 4,11 (2H, q , CH_2)	5,02 (s)				
IVA	5,94 (s)			2,25 (s)	1,09 (3H, t , CH_3), 4,62 (2H, q , CH_2)	8,41 (s)	3,13 (trans) 3,22 (cis)	5-CH_3	6-CH	21
								NCH_3-cis	N=CH	22
								NCH_3-trans	N=CH	5
								5-CH_3	CH_2CH_3	0
								OCH_2	NCH_3-trans	2
VI	6,33 (s)	6,80 (br.s)	12,40 (br.s)	7,58 (3H,m, C_3H_3) 7,78 (2H,m, C_2H_2)						
VII	6,65 (s)			7,50 (3H,m, C_3H_3) 8,14 (2H,m, C_2H_2)	1,15 (3H, tr, CH_3) 4,66 (2H, q , CH_2)	8,45 (s)	3,15 (trans) 3,23 (cis)	C_3H_3	C_2H_2	9
								CH_3	NCH_3-trans	6
								CH_3	NCH_3-cis	4,7
								CH_2	NCH_3-trans	6
								CH_2	NCH_3-cis	4
								NCH_3-trans	N=CH	3
								NCH_3-cis	N=CH	25

TABLE 1 (continued)

Compound	6-CH	2-NH_2, NH	4-NH (S)	5-C-CH_3 5-C-Ph	7-C-OCH_2CH_3 $C(O)OCH_2CH_3$ 7-C-Ph	N=CH	$N(CH_3)_2$ (3H, s, CH_3)	Overhauser effect		
								irradiated signal	response signal	%
1	2	3	4	5	6	7	8	9	10	11
IXa	7,38 (s)	7,15 (br.s)		2,63 (3H, s, CH_3)	7,60 (3H, m, C_3H_3) 7,97 (2H, m, C_2H_2)					
IX6	7,46 (d)	7,28 (br. s)		8,74 (d) $J_{5\text{-}CH,6\text{-}CH}$ = 4,8	7,61 (3H, m, C_3H_3) 8,04 (2H, m, C_2H_2)					
X	7,40 (s)			2,64 (3H, s, CH_3)	7,61 (3H, m, C_3H_3) 8,00 (2H, m, C_2H_2)	8,13 (s)	3,03 (trans) 3,09 (cis)	NCH_3-trans NCH_3-cis C_2H_2 C_2H_2 C_2H_2 C_2H_2 6-CH 6-CH 6-CH	N=CH N=CH 6-CH C_3H_3 NCH_3-trans NCH_3-cis C_2H_2 NCH_3-trans NCH_3-cis	4 18 13 8 3 2,6 14 3 2,5
XV		7,45 (s)	11,27 (1H, d, NH) 12,05 (1H, s, pyrazole NH)		1,23 (3H, tr , CH_3) 1,27 (3H, tr , CH_3) 4,13 (2H, q , CH_2) 4,22 (2H, q , CH_2)	8,55 (d) $^3J_{NH,CH}$ = 13,5				

TABLE 2. Data of ^{13}C NMR Spectra for Pyrazolopyrimidines IIA and IVA, δ, ppm, SSCC (J, Hz)

Compound	2-C	3-C	3a-C	5-C	6-C
IIA	151,5 (narrow m) $^2J_{2\text{-C,NH}_2}$ = 4,5 $^4J_{2\text{-C,NH}}$ = 1*	108,2 (highly br.s.) $^3J_{3\text{C,NH}_2}$ = 2,0*	140,1 (br.s) $^2J_{3\text{aC,NH}}$ = 1,2*	150,6 (m) $^2J_{5\text{-C,CH}_3}$ = 6,2 $^2J_{5\text{-C,CH}}$ = 2,6 $^2J_{5\text{-C,NH}}$ = 1,8*	102,7 (d.q) $^1J_{6\text{-CH}}$ = 172,4 $^3J_{6\text{-C,CH}_3}$ = 4,6
IVA	155,6 (d) $^3J_{2\text{C,N=CH}}$ = 1,4	111,1 (low-intens. s)	146,4 (s)	155,8 (m)	103,4 (d.q) $^1J_{6\text{-CH}}$ = 167,4 $^3J_{6\text{-C,CH}_3}$ = 3,8

Compound	7-C	5-CH_3	N—C=N	OCH_2CH_3	$N(CH_3)_2$
IIA	154,2 (br.s) $^2J_{7\text{-C,CH}}$ = 1,4	19,2 (q.d) $^1J_{CH_3}$ = 130,5 $^3J_{C,CH}$ = 4,6			
IVA	164,0 (m)	24,1 (q.d) $^1J_{CH_3}$ = 127,5 $^3J_{C,CH}$ = 3,0	161,3 (d.m) $^1J_{CH}$ = 188,5	13,6 (q.t) $^1J_{CH_3}$ = 127,5 43,3 (t.q) $^1J_{CH_2}$ = 145,7	34,8 cis (q.m) $^1J_{CH_3}$ = 139,6 41,1 trans (q.m) $^1J_{CH_3}$ = 140,0

*The SSCC values, denoted by *, were determined as a change in signal width by half its height ($l_{1/2h}$) in going from the spectrum recorded in the regime without proton suppression to the spectrum recorded in the selective decoupling regime.

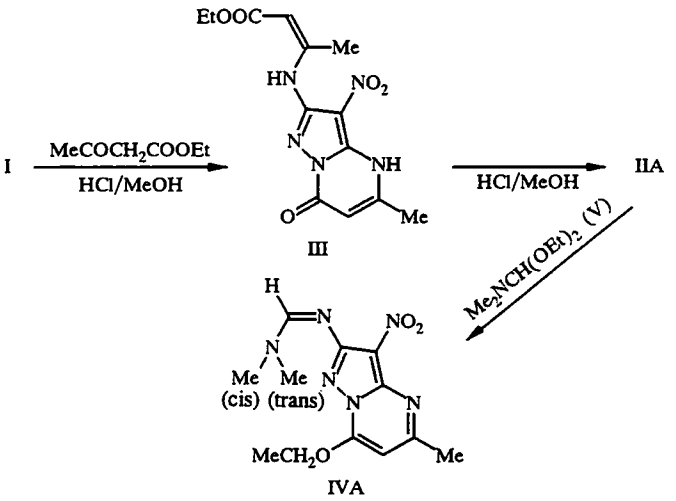
TABLE 3. Physicochemical Properties of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	M^+	Yield, %
		C	H	N			
IIA	$C_7H_7N_5O_3$	40.28 / 40,19	3.33 / 3,34	33.56 / 33,49	>290	209	96
III	$C_{14}H_{17}N_5O_5$	50.42 / 50,14	5.15 / 5,07	20.79 / 20,89	220...245 dec.	335	73
IVA	$C_{12}H_{16}N_6O_3$	49.27 / 49,31	5.62 / 5,49	28.63 / 28,76	212...214	292	56
VI	$C_{12}H_9N_5O_3$	53.28 / 53,13	3.38 / 3,32	25.64 / 25,83	>290	271	93
VII	$C_{17}H_{18}N_6O_3$	57.48 / 57,62	5.24 / 5,08	23.52 / 23,73	188...191	354	64
IXa	$C_{13}H_{11}N_5O_2$	57.17 / 58,17	4.02 / 4,09	26.34 / 26,02	>290	269	86
IXb	$C_{12}H_9N_5O_2$	56.81 / 56,47	3.37 / 3,53	27.41 / 27,45	>290	255	83
X	$C_{16}H_{16}N_6O_2$	59.36 / 59,25	4.82 / 4,93	25.87 / 25,92	207...209	324	79
XII	$C_{12}H_{13}N_5O_3$	52.41 / 52,36	4.78 / 4,72	25.38 / 25,45	>290	275	89
XIII	$C_{15}H_{18}N_6O_3$	54.61 / 54,54	5.38 / 5,54	25.37 / 25,45	276...278	330	75
XV	$C_{11}H_{15}N_5O_6$	42.24 / 42,17	4.81 / 4,79	22.53 / 22,36	242...246	313	94
XVI	$C_{10}H_{11}N_5O_6$	40.48 / 40,40	3.61 / 3,70	23.41 / 23,56	246...248	297	84

of a new, fairly complex compound and the unusual reaction conditions required definitive evidence of the structure of the compound obtained, and structure II was studied by the methods of ^1H NMR spectroscopy and ^{13}C. The ^1H NMR spectrum of compound IIA was fairly simple (Table 1). An experiment involving the overhauser effect (OE) showed that irradiation of

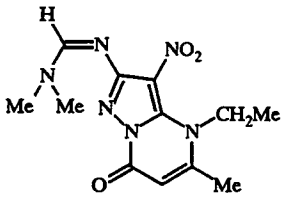
the methyl group signal (2.36 ppm) led to a 19% increase in the vertical intensity of the 6-H proton singlet (5.94 ppm). The reverse experiment (irradiation of the 6-H signal) caused a smaller (3%) but distinct increase in the signal intensity of the 5-CH_3 group protons. These data indicate the spatial proximity of these groups and confirm the pyrazolopyrimidine structure of compound II, but do not help to solve this structure (IIA or IIB). Evidence in favor of structure A is provided by an increase in the methyl group signal (4%) in the presence of irradiation of the 4-NH signal (12.37 ppm). Unfortunately, the reverse OE experiment — irradiation of the signal of CH_3 group protons — did not show a distinct response of the NH signal, possibly owing to a more difficult recording of the change in intensity of the broadened NH signal. A definitive assignment of the structure of the compound studied to IIA was successfully made by studying its ^{13}C NMR spectrum (Table 2).

In the ^{13}C NMR spectrum of pyrazolopyrimidine II, four narrow signals are observed in the weak field region: 108.2 (highly broadened singlet), 140.1 (broadened singlet); 151.8 (narrow multiplet) and 154.2 ppm (broadened singlet). Recording of ^{13}C NMR spectra in the selective decoupling regime made it possible to assign to $C_{(3)}$ carbon the strong-field singlet (108 ppm), which is markedly broadened as a result of the spin-spin interaction with the 2-NH_2 group protons ($^3J_{3\text{-}C,2\text{-}CNH2}$ = 2.0 Hz). The singlet at 140.1 ppm, which narrows on decoupling of the NH proton (12.37 ppm), corresponds to the $C_{(3a)}$ carbon atom ($^2J_{3a\text{-}C,NH}$ = 1.2 Hz). The narrow multiplet at 151.8 ppm is assigned to the $C_{(2)}$ carbon atom, for which an interaction with protons of both 2-NH_2 ($^2J_{2\text{-}C,NH2}$ = 4.5 Hz) and NH ($^4J_{2\text{-}C,NH}$ = 1.0 Hz) is observed. The broadened singlet at 154.2 ppm corresponds to the carbonyl-group carbon, for which a weak spin-spin interaction with the adjacent 6-H proton ($^2J_{7\text{-}C,6\text{-}CH}$ = 1.4 Hz) is observed, and no spin-spin interaction with the NH proton (12.37 ppm) is detected. Of interest is a study of the signal of the carbon atom to which the methyl group is attached. In the spectrum, the signal of this carbon in the form of a multiplet is observed at 150.6 ppm. Subsequent selective decoupling of the signal of the methyl group (2.36 ppm) and 6-H proton (5.94 ppm) made it possible to determine the values of the hetero constants $^2J_{5\text{-}C,CH3}$ = 6.3 Hz and $^2J_{5\text{-}C,6\text{-}CH}$ = 2.6 Hz. The experiment with suppression of the NH-proton signal led to an appreciable narrowing of this multiplet; this indicates a spin-spin interaction of the $C_{(5)}$ carbon with NH ($J_{5\text{-}C,NH}$ = 1.8 Hz), which clearly points to structure IIA.

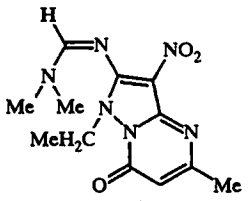


It is understandable that the structure of the intermediate III is also determined by structure IIA. Among the characteristics of the spectrum of compound III (see Table 1), one can include the very weak-field position of the proton signal of the NH substituent in the 2 position (11.80 ppm), indicating the presence of a fairly strong intramolecular hydrogen bond.

Interesting results were obtained in a study of the reaction of pyrazolopyrimidine IIA with dimethylformamide diethylacetal (V). It was found that in addition to the formation of an amide fragment with the participation of the primary amino group in the 2 position of the bicyclic compound, ethylation also takes place in this case. The alkylating properties of amide acetals, in particular, those of acetal V, are well known [5], and the N-alkylation of pyrimidines has been described in the literature [6]. In view of the fact that the pyrimidine NH group of compound IIA is sterically screened by the presence of the nearby groups 5-CH_3 and 3-NO_2, one could, in principle, have expected the formation of two possible types of compounds IVb and IVc, in which ethylation would occur at the $N_{(4)}$ or $N_{(1)}$ atom. Examination of the ^{13}C NMR spectrum of this compound (see Table 2) shows that it lacks the carbonyl carbon atom, and hence, the alkylation by acetal V of compound IIA selectively takes place at the carbonyl oxygen atom in the 8 position. The fact that the compound studied is an O-ethyl derivative is indicated by the value of the direct SSCC $^1J_{CH2}$ for methylene protons, 145.7 Hz, which correlates closely with the reported data for the OCH_2 group [7]. During the recording of the ^1H NMR spectrum of compound IVA (see Table 1),



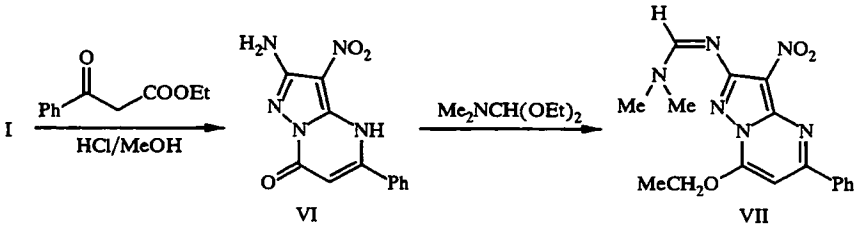
IVB



IVC

an OE experiment for this compound was carried out which showed (as well as for IIA) the spatial proximity of the 5-CH_3 and 6-H protons (irradiation of one group causes an increase in the signal intensity of the other). Irradiation of the signals of the N-CH_3 group of the amide fragment made it possible to establish that the weak-field N-methyl group (3.22 ppm) is cis-oriented relative to the CH-formyl proton (8.41 ppm) — *a* 21% increase in the signal intensity of CH. Correspondingly, the weaker-field N-CH_3 (3.13 ppm) is distant from the CH proton — its irradiation causes only a comparatively small (5%) increase in the signal intensity of N =CH. The OE experiment, carried out for the quartet of methylene protons of the OEt group, showed that its irradiation causes a slight, but distinctly recorded increase in the singlet intensity of the trans-NMe group (3.13 ppm), indicating the spatial proximity of these groups, and confirmed the structure IVA.

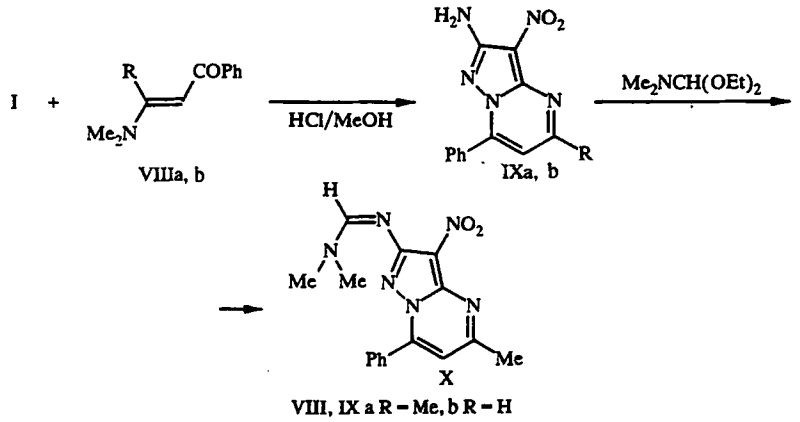
Yet another indication that the pyrazolopyrimidine cyclization involved in the reaction of pyrazole I with acetoacetic ester takes place in the direction of A flows from the fact that the same compound IIA is formed from aminopyrazole I and β-aminocrotonic ester. In this case, the first stage of the process is transamination; this is in good agreement with the known tendency of enamines toward such processes [8]. As in the case of the reaction of compound I with acetoacetic ester, there is also the reaction of I with benzoylacetic ester. In this case, judging from the data of ^1H NMR spectra, compound VI is formed, which on reacting with acetal V is transformed to ethoxyamidine VII.



VI VII

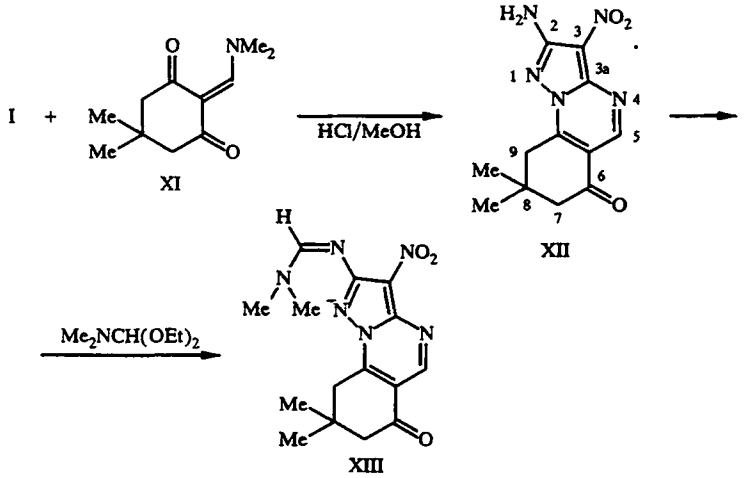
The OE experiment, carried out for amidine VII, showed a small but clearly detectable response of the NMe_2 group on irradiation of the protons of the CH_2O ethyl fragment (see Table 1).

As was pointed out above, cyclization reactions of this type are also entered into by "hidden" β-dicarbonyl compounds, i.e., enamino ethers and enamino ketones. It follows from general considerations that under these conditions, the initial process is transamination, the next step being cyclization. The reaction of compound I with α-dimethylaminoethylideneacetophenone (VIIIa) yields the bicyclic compound IXa, which is converted into amidine X by reaction with acetal V. A comparison of the position in the spectrum of the protons of the dimethylamino groups and meso protons of the amidine fragments in compounds II and X shows that in the latter compound, the signals of these protons are shifted to the weak field (by 0.09-0.13 for NCH_3 and by 0.28 ppm for CH). A comparison of the chemical shifts of the protons of the phenyl ring in the spectra of compounds IXa and X shows a slight weak-field displacement of the multiplet center, corresponding to the meta and para protons for compounds X, with the position of the ortho protons remaining unchanged. The position of the signal of group 5-CH_3 protons in the two compounds is practically the same. These data may indicate the spatial proximity of the amidine fragment and phenyl ring; this determines the structure of compound X (and hence, of the bicyclic compound IX) as a 5-methyl-8-phenyl derivative. A reliable proof of this structure was obtained, as above, by means of the OE experiment. Thus, for compounds X, irradiation of the phenyl ring signals results in a small but clearly recorded increase in the intensity of the signals of the dimethylamino group (see Table 1), and this definitely confirms the structures shown below:



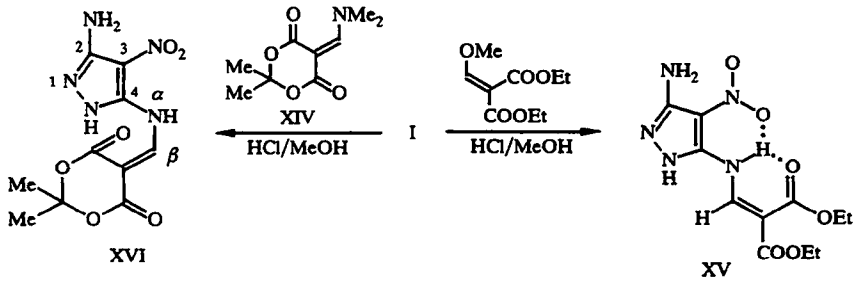
VIII, IX a R = Me, b R = H

Similarly, pyrazolopyrimidine IXb was synthesized from compounds I and VIIIb. 2-Dimethylaminomethylene dimedone (XI) was made to undergo a similar reaction [9] to form the bicyclic compound XII and then amidine XIII.



The ^{1}H NMR spectra of the heterocyclic derivatives obtained and the OE data are presented in the Experimental section.

Particular attention should be paid to the reaction of pyrazole I with ethoxymethylenemalonic ester and 5-dimethylaminomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione (XIV) [8]. The first stage of the reaction between pyrazole I and



ethoxymethylenemalonic ester or the Meldrum acid derivative XIV, as expected, takes place at the primary amino group with the formation of the open compounds XV and XVI, respectively. In contrast to the examples described above, noncyclic reaction products were isolated in these cases. Moreover, it should be noted that pyrimidine cyclization could not be achieved for them under either ordinary or more severe conditions.

The structure of compounds XV and XVI clearly follows from the data of the ^{1}H NMR spectra (see Table 1 for XV and the Experimental section for XVI). Both compounds are characterized by the presence of a fairly strong intramolecular hydrogen bond involving the proton of the NH enamine group and the carbonyl of the ester fragment.

Thus, the above data indicate that the reaction of diaminonitropyrazole I with β-dicarbonyl and enaminocarbonyl compounds takes place regioselectively with the participation of a primary amino group in the first step and subsequent cyclization to substituted pyrazolopyrimidines. The presence in the latter of functional substituents such as the nitro, primary amino, and in several cases, carbonyl group makes these compounds promising starting materials for the preparation of various derivatives of this heterobicyclic system.

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer spectrometer for suspension in Vaseline oil, and the NMR spectra were recorded on an Oxford Unity 400 spectrometer with TMS as the internal standard. The mass spectra were obtained on a Varian SSQ-700 spectrometer with direct injection of the substance into the ion source. The purity of the compounds obtained and the course of the reaction were monitored by means of TLC on Silufol UV-254 plates.

3-Amino-4-nitropyrazolo[1,5-*a*]pyrimidines (IIA, VI, IXa,b) and 3-Amino-4-nitro-6-oxo-8,8-dimethyl-7,9-dihydropyrazolo[1,5-*a*]quinazoline (XII), 3-Dimethoxymethyleneamino-5-amino-4-nitropyrazole (XV) and 3-(2,2-Dimethyl-1,3-dioxane-4,6-dione)methyleneamino-5-amino-4-nitropyrazole (XVI). To a suspension of 1 ml of 3,5-diamino-4-nitropyrazole in 10 ml of ethanol is added 2 mmole of β-dicarbonyl compound, and the mixture is heating to boiling. To the boiling reaction mass 1 ml of 9% HCR/MeOH is added dropwise with vigorous stirring. The reaction mass is kept boiling for 2-3 h and cooled to room temperature, and the yellow precipitate of pyrazolopyrimidine obtained is filtered off, then washed with water, methanol, and ether. The substance obtained is crystallized from DMFA. ^{1}H NMR spectrum for XII (DMSO-D_6): 8.97 (1H, s, 5-H); 7.50 (2H, br. s, 2-NH_2); 2.59 (2H, s, 7-CH_2); 3.20 (2H, s, 9-CH_2); 1.10 ppm (6H, s, 8-$(CH_3)_2$). ^{1}H NMR spectrum for XVI (DMSO-D_6): 12.35 (1H, br. s, pyrazole NH); 11.72 (1H, d, α-NH); 8.66 (1H, d, $^3J_{NH,CH}$ = 14 Hz, β-CH); 7.56 (2H, br. s, 2-NH_2); 1.68 ppm (6H, s, C-$(CH_3)_2$).

3-(α-Methyl-β-ethoxycarbonyl)vinylamino-4-nitropyrazolo[1,5-*a*]pyrimidine (III). The synthesis is carried out as above for compound IIA without heating, and the reaction mass is left standing for one day at 20°C. The bright-yellow precipitate is filtered off and crystallized from an absolute alcohol–DMFA mixture.

3-(Dimethylaminomethylene)amino-4-nitropyrazolo[1,5-*a*]pyrimidines (IVA, VII, X, XIII). To a suspension of 10 mmole of pyrazolopyrimidine in ethanol is added 5 ml (34 mmole) of dimethylformamide diethylformamide diethylacetal, and the mixture is boiled for 1 h. The reaction mass is evaporated under vacuum down to an oily residue which is ground up with a 1:1 ether–alcohol mixture until a yellow crystalline substance is obtained, which is crystallized from methanol. ^{1}H NMR spectrum for XIII (DMSO-D_6): 9.00 (1H, s, 5-H); 8.37 (1H, s, 2-H=CH); 2.61 (2H, s, 7-CH_2); 3.30 (2H, s, 9-CH_2); 3.18 (3H, s, NCH_3-cis); 3.10 (3H, s, NCH_3-trans); 1.12 ppm (6H, s, 8-$(CH_3)_2$). OE experiment (irradiated signal/response signal, %): NCH_3-cis/2-N=CH/20; NCH_3-trans/2-N=CH/2.5; 8-$(CH_3)_2$/7-CH_2/6.5; 8-$(CH_3)_2$/9-CH_2/6.0.

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