pound was similarly obtained, except that $PdCl_2$ was used as the metal salt. The product was purified by extraction and was obtained in 43% yield as fine needles that were soluble in concentrated H_2SO_4, chloroform (with heating), DMSO, and DMF, less soluble in benzene, and insoluble in water; the product had mp 384°C (in air) and 400°C (in a nitrogen atmosphere). Found: C 57.6; H 3.2; N 22.0; Pd 17.4%; M^+ 622. $C_{30}H_{20}N_{10}Pd$. Calculated: C 57.5; H 3.2; N 22.3; Pd 17.0%; M 626.9.

[4,15-Dihydro-1-methyl-3-phenyl-3H-dibenzo[c,m]pyrazolo[3,4-f]quinoxalino[2,3-j][1,2,-5,8,9,12]hexaazacyclotetradecenato(2-)-N^4,$N^{9(10)}$,N^{15},$N^{22(23)}$]copper (VIIIc). This compound was similarly obtained, except that $CuCl_2$ was used as the metal salt. The product was recrystallized from CCl_4 and was obtained in 25% yield; it melted above 300°C. Found: C 61.8; H 3.4; Cu 11.0; N 23.7%; M^+ 583. $C_{30}H_{20}CuN_{10}$. Calculated: C 61.7; H 3.4; Cu 10.9; N 24.0%; M 584.1.

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3-NITRO-1,2,4-TRIAZOL-5-ONE DERIVATIVES

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UDC 547.792.5

3-Nitro-1,2,4-triazol-5-one and its monomethyl derivatives react with methyl vinyl ketone to give products of addition to the ring N_1 and N_4 atoms. The reaction with formaldehyde and N-methylolacetamide proceeds only at the N_1 atom. The keto derivatives of 3-nitro-1,2,4-triazol-5-one undergo the Schmidt reaction to give the corresponding acetamides. A number of compounds that include functional groups in the N_1-alkyl substituent of the 3-nitro ring were obtained by treatment of the bases of N_1-substituted 3,5-dinitro-1,2,4-triazoles in aprotic media.

The biological activity of 1,2,4-triazol-5-one derivatives has been noted [1-3]. Modification of their properties can be achieved by varying the substituents attached to the ring carbon and nitrogen atoms. In particular, the nitration of 1,2,4-triazol-5-one leads to 3-nitro-1,2,4-triazol-5-one [4-6], while alkylation of the latter leads to its mono- or disubstituted derivatives [6-9]. In addition, 1-R-3-nitro-1,2,4-triazol-5-ones were obtained in the reaction of 1-R-3,5-dinitro-1,2,4-triazoles with hydroxylamine [10] or were isolated as side products in their reactions with other nucleophilic reagents [10, 11].

In the present research we used both variants, viz., the reaction of NH acids of the triazolone series with electrophilic reagents and substitution at the C_5 atom in 1-R-3,5-di-

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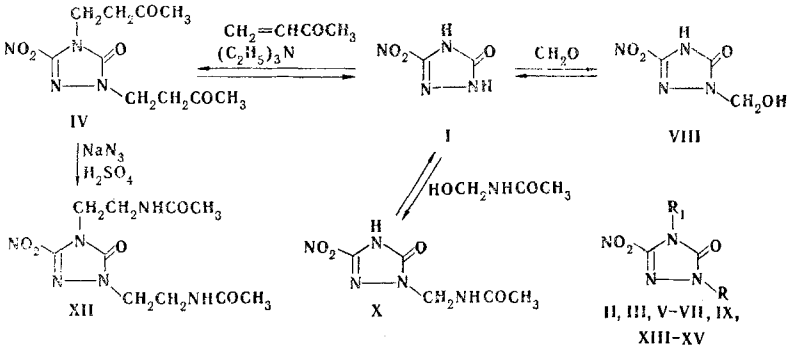
nitro-1,2,4-triazoles or 1-R-3-nitro-5-bromo-1,2,4-triazoles, to obtain 3-nitro-1,2,4-triazol-5-one derivatives that include functional groups in the N-alkyl substituents.

3-Nitro-1,2,4-triazol-5-one (I) and its 1- and 4-methyl-substituted derivatives (II and III) react with methyl vinyl ketone (MVK) in dimethylformamide (DMF) in the presence of bases upon heating to give the corresponding N-(3'-oxobutyl)-3-nitro-1,2,4-triazolones (IV-VI). The condensation does not take place in the absence of a catalyst or at room temperature in DMF. An attempt to use other solvents (acetone, dioxane, alcohols, and acetonitrile) was unsuccessful, which may be explained by the very low solubility in them of the starting triazolones I-III. We were unable to isolate products of monoaddition (N_1 or N_4 isomers) in the case of the reaction of triazolone I with MVK, although its controllable methylation gives monosubstitution products in satisfactory yields [9]. Diketone IV was obtained in the case of an equimolar reagent ratio and when a large excess of triazolone I was used. We were able to synthesize one of the possible isomers, viz., adduct VII, from 1-(3'-oxobutyl)-3,5-dinitro-1,2,4-triazole by replacement of the nitro group in the 5 position of the ring by the hydroxide anion. Ketone VII undergoes virtually complete conversion to diketone IV when the general method of condensation of triazolones with MVK is used.

An attempt to realize the reaction of triazolones I-III with reagents that are less reactive than MVK such as acrylonitrile and methyl acrylate under various conditions was unsuccessful.

A comparison of the experimental data on the synthesis of ketones of the triazolone and triazole series [12] shows that 3-nitro-5-R-1,2,4-triazoles are more active in the Michael reaction than 3-nitro-1,2,4-triazol-5-ones, which have comparable acidities. This constitutes evidence for the higher nucleophilicity of the N_1 atom in the case of the conjugated triazole system.

Triazolone I undergoes reaction with formaldehyde and N-methylolacetamide in the absence of catalysts (in contrast to the reaction with MVK) but gives only monosubstitution products (VIII, X). The introduction of bases and raising the temperature shift the equilibrium to favor the starting compounds. Replacement of a proton-donor solvent (water) by an aprotic solvent (acetone) increase the yield of hydroxymethyl derivative VIII from 50% to 85%, which is probably due to its higher thermodynamic stability under these conditions. Monomethylated triazolones II and III do not react in water with formaldehyde. The hydroxymethylation of 3-nitro-4-methyl-1,2,4-triazol-5-one takes place in 80% acetone to give 1-hydroxymethyl-3-nitro-4-methyl-1,2,4-triazol-5-one (IX) in 60% yield. We were unable to isolate the product of the reaction in the reaction mass in small amounts was established chromatographically and by means of PMR spectroscopy (δ_{CH_2} 5.40 ppm).



II R=CH_3, R_1=H; III R=H, R_1=CH_3; V R=CH_3, R_1=$CH_2CH_2COCH_3$; VI R=$CH_2CH_2COCH_3$, R_1=CH_3; VII R=$CH_2CH_2COCH_3$, R_1=H; IX R=CH_2OH, R_1=CH_3; XIII R=CH_3, R_1=$CH_2CH_2NHCOCH_3$; XIV R=$CH_2CH_2NHCOCH_3$, R_1=CH_3; XV R=$CH_2CH_2NHCOCH_3$, R_1=H

The fact that hydroxymethylation in monosubstituted 3-nitro-1,2,4-triazolones II and III proceeds successfully only when substitution is possible only at the N_1 atom of the triazole ring (III) makes it possible to assign N_1 derivative structures (VIII, X) to the products of the reaction of triazolone I with formaldehyde and methylolacetamide. The results indicate a substantial difference in the nucleophilicity of the N_1 and N_4 atoms in triazolone I and its monomethyl derivatives II and III, which is in agreement with the data on their acidities [9].

TABLE 1. 1-R-3-Nitro-4-R_1-1,2,4-triazol-5-ones

Compound	R	R_1	mp, [a] °C	IR spectra, cm^{-1}
1	2	3	4	5
IV	$CH_2CH_2COCH_3$	$CH_2CH_2COCH_3$	90—91	810 m, 880 w, 500 m, 1070 m, 1135 m, 1175 m, 1180 m, 1260 m, 1310 m, 1350 m, 1370 m, 1440 m, 1470 m, 1550 m, 1725 s
V	CH_3	$CH_2CH_2COCH_3$	102—103	810 s, 890 m, 1040 m, 1060 m, 1135 m, 1170 m, 1195 m 1270 s, 1345 s 1365 m, 1380 w, 1400 w, 1440 s, 1455 s, 1540 m, 1560 m, 1710 vs, 1725 s,
VI	$CH_2CH_2COCH_3$	CH_3	55—56	830 m, 920 m, 1070 w, 1150 m, 1180 m, 1260 m, 1290 m, 1320 vs, 1410 m, 1540 m, 1710 vs 1730 vs
VIII	CH_2OH	H	110—112	710 s, 720 s, 730 s, 800 m, 860 s, 890 w, 1000 s, 1050 vs, 1110 w, 1150 w, 1170 w, 1280 w, 1310 w, 1320 w, 1360 w, 1450 m, 1480 w, 1550 s 1710 s, 3400 m
IX	CH_2OH	CH_3	88—89	730 m, 750 m, 760 m, 810 s, 900 m, 1000 w, 1050 w, 1110 w, 1170 m, 1320 s, 1360 w, 1450 m, 1550 vs, 1720 vs, 3400 m,
X	$CH_2NHCOCH_3$	H	120—121	720 m 780 m, 810 m, 840 w, 900 w, 990 m, 1130 m, 1200 m, 1260 w, 1310 w, 1390 w 1420 s, 1580 w, 1640 s, 1720 vs
XII	$CH_2CH_2NHCOCH_3$	$CH_2CH_2NHCOCH_3$	80—82	730 m, 810 m, 900 w, 980 m 1010 m, 1170 m, 1220 m, 1310 m, 1330 w, 1370 w, 1380 w, 1420 m, 1520 w, 1600 m, 1710 s
XIII	CH_3	$CH_2CH_2NHCOCH_3$	165—166	730 w, 800 m, 900 m, 1020 w, 1130 w, 1200 w 1250 m, 1300 m, 1350 m, 1370 m, 1410 m, 1520 s, 1620 m, 1710 vs
XIV	$CH_2CH_2NHCOCH_3$	CH_3	207—208	730 w, 810 w, 920 w, 1010 w, 1080 w, 1120 w, 1180 w 1200 w, 1450 w, 1530 m, 1710 s
XV	$CH_2CH_2NHCOCH_3$	H	128—130	740 w, 810 сл, 1010 m, 1150 vs, 1310 w, 1330 w, 1370 m, 1480 w, 1540 m, 1630 m, 1700 s
XXIV	CH_2COOCH_3	H	181—182	850 w, 885 w, 1020 m, 1090 m, 1150 m, 1250 m, 1320 w, 1460 m, 1520 m, 1560 m, 1715 s, 1750 s
XXV	$CH_2CH(ONO_2)CH_3$	H	194—195	720 m, 750 m, 760 s, 810 vs, 900 vs, 930 w, 1050 m, 1100 m, 1190 m, 1260 vs, 1280 s, 1370 s, 1390 m, 1550 vs, 1590 w, 1650 vs, 1730 vs
XXVI	$CH_2CH=CH_2$	H	188—189	730 m, 810 m, 950 m, 990 w, 1050 w, 1120 w, 1170 w,

PMR spectra, ppm				Found, %			Empirical formula	Calc., %			M		Yield, %
тр-CH_2	CO—CH_3	тр-CH_3	others	C	H	N		C	H	N	found[b]	calc.	
6	7	8	9	10	11	12	13	14	15	16	17	18	19
4,12 t (2H); 4,30 t (2H); J=6Hz	2,18 s (3H), 2,20 s (3H)	—	CH_2CO: 3,00 t (2H); 3,30 t (2H); J=6 Hz	44,7	5,1	21,0	$C_{10}H_{14}N_4O_5$	44,5	5,2	20,3	275	270	85
4,27t (2H); J=1 Hz	2,11 s (3H)	3,50 s (3H)	CH_2CO: 3,00 t (2H); J=4 Hz	39,4	4,9	26,3	$C_7H_{10}N_4O_4$	39,3	4,6	26,2	216	214	80
4,27t (2H); J=4 Hz	2,15 s (3H)	3,58 s (3H)	CH_2CO: 3,00 t (2H); J=4 Hz	39,4	4,8	26,2	$C_7H_{10}N_4O_4$	39,3	4,6	26,2	219	214	82
5,40 s (2H)	—	—	NH: 7,3 Hz (1H); OH: 6,0 br (1H)	22,3	2,3	35,3	$C_3H_4N_4O_4$	22,5	2,5	35,0	150	156	85
5,30 s (2H)	—	3,56 (3H)	OH: 5,6 br (1H)	27,3	3,5	32,4	$C_4H_6N_4O_6$	27,6	3,4	32,2	171	174	60
5,30 d (2H); J= =4 Hz	1,85 s (3H)	—	NH: 7,0 br (1H)	28,8	3,7	34,3	$C_5H_7N_5O_4$	29,0	3,5	34,5	205	201	53
3,95 t (2H); 4,25t (2H); J=6 Hz	1,80 s (3H), 1,83 s (3H)	—	CH_2NH: 3,45 t (4H)d; NH: 7,0 br (2H)	40,2	5,3	28,0	$C_{10}H_{16}N_6O_5$	40,0	5,3	28,0	312	300	40
4,15t (2H); J=6 Hz	1,72 s (3H)	3,50 c (3H)	CH_2NH: 3,40 t (2H); NH: 7,0 br (1H)	36,4	4,5	30,3	$C_7H_{11}N_5O_4$	36,7	4,8	30,6	219	229	85
4,17 t (2H); J=6 Hz	1,80 s (3H)	3,58 s (3H)	CH_2NH: 3,50 t (2H); J=6 Hz NH: 7,0 br (1H)	36,5	4,7	30,4	$C_7H_{11}N_5O_4$	36,7	4,8	30,6	221	229	45
3,90t (2H); J=4 Hz	1,80 s (3H)	—	CH_2NH: 3,45 t (2H), J=4 Hz; NH: 6,7 br (1H)	33,1	4,0	32,4	$C_6H_9N_5O_4$	33,1	4,0	32,4	210	215	70
4,60 s (2H)	3,80 s (3H)	—	—	29,7	2,1	27,6	$C_5H_6N_4O_5$	29,8	2,1	27,6	210	202	68
5,10 d (2H); J=7 Hz	—	—	CH—CH_3: 6,50 m (1H); 3,30 d (3H); J=7 Hz	30,3	4,7	25,6	$C_5H_7N_5O_6$	30,0	3,0	25,8	237	233	63

TABLE 1 (continued)

1	2	3	4	5
				1260 w, 1280 m, 1360 s, 1450 m, 1460 m, 1560 w, 1580 w, 1690 vs, 1730 vs

[a]The compounds were crystallized: IV-VI from butanol, VIII dioxane–chloroform, XII-XVI from ethanol, and XXV and XXVI acetone. [c]Splitting of the signal due to spin–spin coupling two CH_2 groups merge.

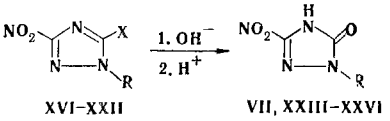
Primarily ionization at the less basic N_4 atom (pK_A 3.76 and 11.25 in the 4 and 1 positions, respectively) and, consequently, the addition of MVK to the N_4 atom occur in the presence of catalytic amounts of base in the reaction of triazolone I with MVK. The ionization of the intermediate monoadduct* ensures its rapid consumption in the reaction with MVK, since the reaction in the second step takes place at the more nucleophilic center. The absence of a product of monoaddition of MVK to triazolone I can be explained by the slow formation of a monoadduct and its rapid reaction with a second molecule of MVK.

Attack by the electrophilic reagent only at the most nucleophilic N_1 atom is realized in reactions that take place in the absence of bases (in the reaction with formaldehyde and methylolacetamide), while substitution at the N_4 atom does not occur either in view of its low reactivity or because of the thermodynamic instability of the resulting compounds.

In the absence of a nitro group in the 3 position of the 3-triazolone ring hydroxymethylation takes place at both nitrogen atoms to give 1,4-dihydroxymethyl-1,2,4-triazol-5-one (XI), which constitutes evidence for the substantial effect of an acceptor substituent in a position adjacent with respect to the reaction center on its nucleophilicity.

Expansion of the series of derivatives of 3-nitro-1,2,4-triazolone can be achieved by chemical transformations of compounds that include functional groups in the N-alkyl substituents. Thus when ketones IV-VII were subjected to the Schmidt reaction with sodium azide in 100% sulfuric acid, a number of amides (XII-XV) were obtained in satisfactory yields. A comparison of the signals of the protons of the methyl and methylene groups in the PMR spectra of amides XII-XV and their precursor ketones XIX-XX and IV and VII shows that the signal of the methyl group is shifted to strong field when an NH fragment is introduced, whereas the signal of the methylene group is shifted to weak field (Table 1). The same changes in the PMR spectra were observed on passing from ketones of the triazole series to triazolylacetamides [12, 13], which makes it possible to assign acetamide structures to XII-XV rather than the isomeric amides of triazole-5-ketopropionic acids.

A number of 1-R-3-nitro-1,2,4-triazolones that include functional groups in the alkyl substituent were obtained by the reaction of the corresponding 1-R-3,5-dinitro- and 1-R-3-nitro-5-bromo-1,2,4-triazoles with bases in aprotic solvents (acetone and dioxane).



XVI-XXII VII, XXIII-XXVI

XVI X=NO_2, R=$CH_2CH_2COCH_3$; XVII X=NO_2, R=CH_2COCH_3; XVIII X=Br, R=CH_2COCH_3; XIX X=NO_2, R=CH_2COOCH_3; XX X=Br, R=CH_2COOCH_3; XXI X=Br, R=$CH_2CH(ONO_2)CH_3$; XXII X=NO_2, R=$CH_2CH=CH_2$; XXIII R=CH_2COCH_3; XXIV R=CH_2COOCH_3; XXV R=$CH_2CH(ONO_2)CH_3$; XXVI R=$CH_2CH=CH_2$

Although this method makes it possible to obtain triazolone derivatives, the synthesis of which was not possible by substitution at the nitrogen atom in structures I-III, it is expedient to use it only for compounds in which the ring heteroatom–substituent bond is not subject to the action of bases. If this were not the case, in addition to substitution at the C_5 atom of the ring one would observe side processes associated with transformations at the N_1 atom, and their contribution would turn out to be predominant. Thus in the case of ketone XVI the yield of triazolone VII does not exceed 10-15% due to realization of a reverse Michael reaction both in the starting compound and in the desired product.

*The pK_A value of 4-methyl-3-nitro-1,2,4-triazol-5-one is 6.50 [9], which is probably close to the values for other N_4-substituted 3-nitro-1,2,4-triazol-5-ones.

6	7	8	9	10	11	12	13	14	15	16	17	18	19
4,35 d (2H); $J=7$ Hz	—	—	$CH=CH_2$: 4,55 m, 4,35 m; 6,20 m	35,4	3,4	33,2	$C_5H_6N_4O_3$	35,5	3,0	33,1	166	170	72

from dichloroethane, IX from dichloroethane—ethanol, X from from carbon tetrachloride. [b]Reverse ebullioscopy from with NH when D_2O is added — singlet. [d]The signals of the

EXPERIMENTAL

The PMR spectra of solutions of the compounds in hexadeuteroacetone were recorded with a Perkin—Elmer R-12 spectromer (60 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of films of the compounds were recorded with a UR-20 spectrometer.

1(4)-(3'-Oxobutyl)-3-nitro-1,2,4-triazol-5-ones (IV-VI). A 35-mmole sample of triazolone I-III [9] or VII [11] was dissolved in 60 ml of DMF, 3.5 ml of methyl vinyl ketone and 2 ml of triethylamine were added, and the mixture was heated in a flask equipped with a reflux condenser at 80°C for 8 h. It was then cooled, diluted with water, and extracted with ethyl acetate (four 100-ml portions). The solvent was removed, and the residue was crystallized (Table 1).

N-Hydroxymethyl-1,2,4-triazol-5-ones (VII, IX, and XI). An 84-mmole sample of formaldehyde in the form of a 35% solution was added to 21 mmole of triazolone in 30 ml of acetone, and the mixture was stirred at room temperature for 8 h. It was then diluted to twice its original volume and extracted with ethyl acetate (three 30-ml portions). The solvent was evaporated, and the residue was crystallized (see VIII and IX in Table 1). 1,4-Dihydroxymethyl-1,2,4-triazol-5-one (XI), with mp 97-98°C (dichloroethane—ethanol), was obtained in 70% yield. IR spectrum, cm^{-1}: 750 m, 810 w, 850 w, 960 w, 980 w, 1030 m, 1080 m, 1160 m, 1210 m, 1250 w, 1380 m, 1420 w, 1570 m, 1710 vs, and 3400 m. PMR spectrum: δ_{CH_2} 6.25, 6.40; δ_{CH} 7.90 ppm. Found: C 32.6; H 4.6; N 29.4%; M 138. $C_4H_7N_3O_3$. Calculated: C 32.8; H 4.5; N 29.6%; M 144.

1-Acetamidomethyl-3-nitro-1,2,4-triazol-5-one (X). A solution of N-methylolacetamide in 5 ml of ethanol was added to a solution of 3.3 g (25.4 mmole) of triazolone I in 15 ml of ethanol, obtained by fusion of 0.98 g of acetamide with 0.47 g of paraformaldehyde in the presence of traces of potassium hydroxide. The reaction mixture was stirred at room temperature for 8 h and allowed to stand overnight. It was then diluted to twice its original volume with water and extracted with ethyl acetate (three 25-ml portions). The solvent was evaporated, and the residue was crystallized (Table 1).

N-Acetamidoethyl-3-nitro-1,2,4-triazol-5-ones (XII-XV). A 30-ml sample of dry chloroform was added to 35 ml of 100% of sulfuric acid, and 20 mmole of ketone (IV-VII) was added in portions at 10°C. A 23-mmole sample of sodium azide was added to the resulting solution with vigorous stirring at 20°C; each successive portion of the azide was added after gas evolution had ceased. The mixture was then stirred at 20°C for another 4 h, after which the acidic layer was separated and poured into 350 ml of water containing ice. The solution was neutralized with sodium bicarbonate to pH 4-5 and filtered to remove the sodium sulfate, and the filtrate was extracted with ethyl acetate (five 50-ml portions). In the synthesis of amide XV, prior to extraction the filtrate was acidified to pH 1 with 10% H_2SO_4. The solvent was evaporated, and the residue was crystallized from alcohol (Table 1).

1-R-3-Nitro-1,2,4-triazol-5-ones (VII, XXIII-XXVI). A solution of 10.6 mmole of sodium hydroxide in 5 ml of water (or 10.6 mmole of triethylamine) was added to a solution of 10.6 mmole of triazole XVI-XVIII [12], XIX, XX [14], XXI [15], or XXII [16] in 25 ml of acetone (dioxane), and the mixture was maintained at 60°C until the starting material vanished [according to thin-layer chromatography (TLC)]. It was expedient to treat XVIII, XX, and XXI with triethylamine in dioxane at 90°C. The reaction mixture was then cooled, the solvent was evaporated, and the residue was dissolved in 20 ml of water, acidified to pH 1 with 10% H_2SO_4, and extracted with ethyl acetate (three 25-ml portions). The solvent was evaporated, and the residue was crystallized (Table 1). Compounds VII and XXIII were identical to the compounds obtained in [11] and were obtained in 10-15% and 75-80% yields, respectively.

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TETRAZOLES.

9.* ACID–BASE PROPERTIES OF 5-SUBSTITUTED TETRAZOLES

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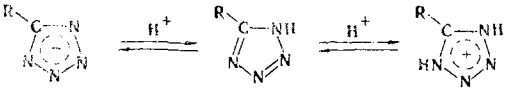
The basicities of series of 5-R-tetrazoles in aqueous solutions of sulfuric acid were studied by UV and PMR spectroscopy. The pK_{BH^+} values of these compound correlate with the σ_p substituent constants. The transmission factor of the p-phenylene ring ($\pi' = 0.23$) was calculated from the ratio of the reaction constants for protonation of substituted 5-phenyltetrazoles and 5-R-tetrazoles. A linear dependence between the pK_a values and the pK_{BH^+} values of 5-substituted tetrazoles was established.

It is known that tetrazoles and 5-substituted tetrazoles are heterocyclic N–H acids with moderate strength. When these compounds are dissolved in mineral acids, they behave like weak organic bases [2].



*See [1] for Communication 8.

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