NITROAZINES.

18.* ARYLATION AND DESTRUCTION OF 6—NITRO—1,2,4—TRIAZOLO[1,5—*a*]PYRIMIDINES

V. L. Rusinov, M. N. Kushnir, O. N. Chupakhin, and G. G. Aleksandrov

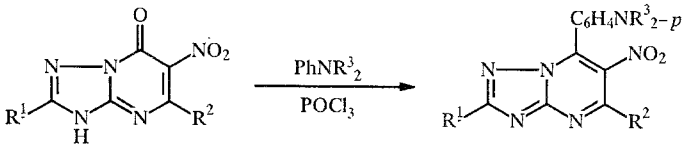
6—Nitro—7—aryl—1,2,4—triazolo[1,5—a]pyrimidines were synthesized by treatment of the corresponding 7—oxo compounds with phosphorus oxychloride in the presence of N,N—dialkylanilines. The 7—(N—methyl—p—methoxyphenylamino) derivatives were formed under the same conditions with N,N—dimethyl—p—anisidine. The nitroarylazolopyrimidines produced underwent destruction to give ω—nitroacetophenones on treatment with water. The influence of substituents on the course of the reaction is shown and the mechanism is discussed.

A general method for the preparation of chlorine substituted heterocyclic compounds from the corresponding oxo derivatives is treatment of the latter with phosphorus oxychloride in the presence of dialkylanilines [2]. A conversion of this type has been described for 5—methyl—6—nitro—7—oxo—1,2,4—triazolo[1,5—*a*]pyrimidine (Ia). According to a patent [3], reaction of a mixture of compound (Ia) and N,N—dimethylaniline (ratio 1:0.75) with phosphorus oxychloride gave 5—methyl—6—nitro—7—chloro—1,2,4—triazolo[1,5—*a*]pyrimidine. We have reported briefly [4] that N,N—dialkylanilines are not inert when this method is adhered to strictly but react with the triazolopyrimidines (I) to give 6—nitro—7—(*p*—N,N,dialkylaminophenyl)triazolo[1,5—*a*]pyrimidines II and III. Formation of compounds of type II under these conditions has been confirmed [5].

The present paper contains more detailed information on the interaction of 6—nitro—7—oxo—1,2,4—triazolo[1,5—*a*]-pyrimidines with dialkylanilines in phosphorus oxychloride, and also on the structure and properties of the compounds obtained.

The formation of compounds II and III in this reaction does not depend on the nature of the substituents in the azole and pyrimidine units, but the presence of a nitro group in position 6 is essential.

The yield of compounds II and III is increased by changing reagent ratio (twofold excess of dialkylaniline) (Table 1).



Ia-d IIa-d, IIIa

I—IIIa R^1 = H, R^2 = Me; b R^1 = Et, R^2 = Me; c R^1 = CF_3, R^2 = Me; d R^1 = Ph, R^2 = H; II R^3 = Me; III R^3 = Et

In order to exclude the possibility of *p*—substitution in the aryl amine, we attempted to chlorinate the 6—nitro—7—oxo—triazolo[1,5—*a*]pyrimidines Ia and Id (R^1 = Me, R^2 = H) using an aryl amine blocked in the 4 position, N,N—dimethyl—*p*—anisidine, under the same conditions. However substitution of the oxo group of the heterocycle occurred to give the 7—(N—methyl—*p*—methoxyphenylamino) derivatives accompanied by the unusual demethylation of anisidine (see [6]).

*For Communication 17 see [1].

Urals Polytechnical Institute, Ekaterinburg 620002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1546—1554, November, 1992. Original article submitted July 20 1992.

0009-3122/92/2811-1323$12.50

TABLE 1. 6—Nitro—1,2,4—triazolo[1,5—*a*]pyrimidines IIa-d, IIIa, and IVa and b

Compound	Molecular formula	R^1	R^2	mp, °C	Yield, %
IIa	$C_{14}H_{14}N_6O_2$	H	CH_3	240...241	23
IIb	$C_{16}H_{18}N_6O_2$	C_2H_5	CH_3	191...193	21
IIc	$C_{15}H_{13}F_3N_6O_2$	CF_3	CH_3	224...226	35
IId	$C_{19}H_{16}N_6O_2$	C_6H_5	H	251...253	38
IIIa	$C_{16}H_{18}N_6O_2$	H	CH3	188...190	20
IVa	$C_{14}H_{14}N_6O_2$	H	CH_3	209...211	18
IVb	$C_{14}H_{14}N_6O_3$	CH_3	H	205...206	16

TABLE 2. Spectroscopic Characteristics of 6—Nitro—1,2,4—triazolo[1,5—*a*]pyrimidines IIa-d, IIIa and IVa and b

Compound	^{1}H NMR spectra, δ, ppm					IR spectra, cm^{-1}		Mass spectra, m/z (I_{rel}, %)				
	2', 6'-H d	3', 5'-H d	R^1 s	R^2 s	R^3 s	NO_2 sym	NO_2 asym	$[M]^+$	$[M]^{++}$	$[M-OH]^+$	$[M-NO]^+$	$[M-NO_2]^+$
IIa	7,61	6,88	8,75	2,65	3,07	1305	1540	298 (100)	149 (3)	281 (1)	268 (1)	252 (8)
IIb	7,50	6,76	1,27*1, 3,00*2	2,57	3,08	1305	1540	326 (100)	163 (2)	309 (1)	296 (1)	280 (1)
IIc	7,55	6,85	—	2,69	3,08	1300	1540	366 (100)	183 (2)	349 (1)	336 (1)	320 (1)
IId	7,75	6,90	7,42...7,61*3 8,03...8,30*3	9,35	3,09	1300	1515	360 (100)	180 (5)	343 (1)	330 (3)	314 (2)
IIIa	7,58	6,79	8,66	2,63	1,16*1, 3,45*2	1310	1535	326 (55)	163 (2)	—	296 (2)	—
IVa*4	7,29	6,89	8,64	2,53	—	1300	1520	314 (100)	—	297 (25)	284 (5)	268 (7)
IVb*5	7,30	6,85	2,49	9,05	—	1305	1520	314 (100)	—	297 (15)	284 (2)	268 (9)

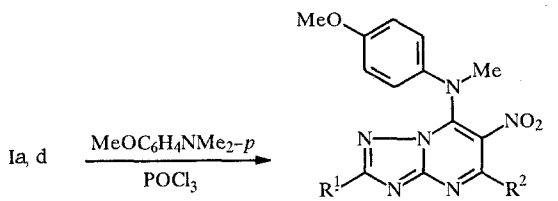
*1 triplet.

*2 quartet.

*3 multiplet.

*4 singlets for the N— and O—methyl group protons at 3.69 and 3.76 ppm.

*5 singlets for the N— and O—methyl group protons at 3.73 and 3.76 ppm.



IVa,b

IVa R^1 = H, R^2 = Me; b R^1 = Me, R^2 = H

$\nu(NO_2)$ bands were identified in the IR spectra of the synthesized nitroazolopyrimidines IIa—d, III, and IVa and b in the 1540—1515 (*asym*) and 1300—1310 cm^{-1} (*sym*) regions.

The most characteristic signals in the ^{1}H NMR spectra of compounds IIa—g are doublets of doublets in the 6.76—6.90 and 7.50—7,61 ppm regions which belong to the protons of the *p*—substituted phenylene unit, the singlets for the dimethylamino group protons at 3.07—3.08 ppm (a triplet and quartet for the protons of the diethylamino group are present in the spectrum of compound IIIa), and the signals of the substituents on the heterocycle. Singlets in the 3.69—3.76 ppm region belonging to the protons of the N— and O—methyl groups were noted for the 7—(methylarylamino) derivatives IVa and IVb.

TABLE 3. Coordinates of Non—hydrogen Atoms ($\times 10^4$) in Molecule IIa

Atom	x	y	z	Atom	x	y	z
$O_{(1)}$	475 (2)	8556 (9)	5664 (7)	$C_{(6)}$	153 (2)	8021 (9)	5460 (7)
$O_{(2)}$	179 (2)	9685 (8)	6153 (7)	$C_{(7)}$	-004 (2)	730 (1)	6290 (8)
$N_{(1)}$	-292 (2)	5894 (9)	6499 (7)	$C_{(8)}$	351 (2)	887 (1)	3447 (8)
$N_{(3)}$	-238 (2)	5989 (9)	4643 (7)	$C_{(10)}$	-034 (2)	7158 (9)	7505 (8)
$N_{(4)}$	048 (2)	7446 (8)	3976 (6)	$C_{(11)}$	147 (2)	6805 (9)	7980 (8)
$N_{(7a)}$	-126 (2)	6687 (8)	5888 (6)	$C_{(12)}$	131 (2)	663 (1)	9120 (8)
$N_{(9)}$	282 (2)	8787 (9)	5789 (7)	$C_{(13)}$	-081 (2)	680 (1)	9811 (8)
$N_{(10)}$	-102 (2)	6655 (9)	10920 (7)	$C_{(14)}$	-264 (2)	717 (1)	9209 (8)
$C_{(2)}$	-348 (2)	551 (1)	5699 (9)	$C_{(15)}$	-245 (2)	734 (1)	8149 (8)
$C_{(3a)}$	-108 (2)	676 (1)	4766 (8)	$C_{(16)}$	089 (2)	622 (1)	11469 (9)
$C_{(5)}$	178 (2)	8050 (9)	4324 (8)	$C_{(17)}$	-333 (2)	669 (1)	11975 (9)

TABLE 4. Bond Lengths (l) in Molecule IIa

Bond	l, Å	Bond	l, Å	Bond	l, Å
$O_{(1)}$—$N_{(9)}$	1,17 (2)	$N_{(7a)}$—$C_{(3a)}$	1,39 (1)	$C_{(6)}$—$C_{(7)}$	1,40 (2)
$O_{(2)}$—$N_{(9)}$	1,24 (1)	$N_{(7a)}$—$C_{(7)}$	1,35 (2)	$C_{(7)}$—$C_{(10)}$	1,49 (1)
$N_{(1)}$—$N_{(7a)}$	1,39 (1)	$N_{(9)}$—$C_{(6)}$	1,44 (2)	$C_{(10)}$—$C_{(11)}$	1,37 (2)
$N_{(1)}$—$C_{(2)}$	1,34 (2)	$N_{(10)}$—$C_{(13)}$	1,36 (1)	$C_{(10)}$—$C_{(15)}$	1,39 (2)
$N_{(3)}$—$C_{(2)}$	1,35 (1)	$N_{(10)}$—$C_{(16)}$	1,50 (2)	$C_{(11)}$—$C_{(12)}$	1,40 (1)
$N_{(3)}$—$C_{(3a)}$	1,32 (2)	$N_{(10)}$—$C_{(17)}$	1,50 (2)	$C_{(12)}$—$C_{(13)}$	1,41 (2)
$N_{(4)}$—$C_{(3a)}$	1,36 (2)	$C_{(5)}$—$C_{(6)}$	1,41 (1)	$C_{(13)}$—$C_{(14)}$	1,40 (2)
$N_{(4)}$—$C_{(5)}$	1,33 (2)	$C_{(5)}$—$C_{(8)}$	1,53 (2)	$C_{(14)}$—$C_{(15)}$	1,42 (1)

TABLE 5. Bond Angles in Molecule IIa

Angle	ω°	Angle	ω°	Angle	ω°
$N_{(7a)}N_{(1)}C_{(2)}$	101,5(9)	$N_{(1)}C_{(2)}N_{(3)}$	116(1)	$C_{(6)}C_{(7)}C_{(10)}$	125(1)
$C_{(2)}N_{(3)}C_{(3a)}$	103(1)	$N_{(3)}C_{(3a)}N_{(4)}$	128(1)	$C_{(7)}C_{(10)}C_{(11)}$	119(1)
$C_{(3a)}N_{(4)}C_{(5)}$	117(1)	$N_{(3)}C_{(3a)}N_{(7a)}$	111(1)	$C_{(7)}C_{(10)}C_{(15)}$	120(1)
$N_{(1)}N_{(7a)}C_{(3a)}$	108,1(9)	$N_{(4)}C_{(3a)}N_{(7a)}$	121(1)	$C_{(11)}C_{(10)}C_{(15)}$	121(1)
$N_{(1)}N_{(7a)}C_{(7)}$	127(1)	$N_{(4)}C_{(5)}C_{(6)}$	122(1)	$C_{(10)}C_{(11)}C_{(12)}$	122(1)
$C_{(3a)}N_{(7a)}C_{(7)}$	125(1)	$N_{(4)}C_{(5)}C_{(8)}$	118(1)	$C_{(11)}C_{(12)}C_{(13)}$	119(1)
$O_{(1)}N_{(9)}O_{(2)}$	124(1)	$C_{(6)}C_{(5)}C_{(8)}$	119(1)	$N_{(10)}C_{(13)}C_{(12)}$	121(1)
$O_{(1)}N_{(9)}C_{(6)}$	119(1)	$N_{(9)}C_{(6)}C_{(5)}$	120(1)	$N_{(10)}C_{(13)}C_{(14)}$	121(1)
$O_{(2)}N_{(9)}C_{(6)}$	117(1)	$N_{(9)}C_{(6)}C_{(7)}$	118(1)	$C_{(12)}C_{(13)}C_{(14)}$	118(1)
$C_{(13)}N_{(10)}C_{(16)}$	121(1)	$C_{(5)}C_{(6)}C_{(7)}$	121(1)	$C_{(13)}C_{(14)}C_{(15)}$	123(1)
$C_{(13)}N_{(10)}C_{(17)}$	121(1)	$N_{(7a)}C_{(7)}C_{(6)}$	113(1)	$C_{(10)}C_{(15)}C_{(14)}$	117(1)
$C_{(16)}N_{(10)}C_{(17)}$	117(1)	$N_{(7)}C_{(7)}C_{(10)}$	121(1)		

TABLE 6. Atomic Coordinates ($\times 10^4$ for O, N, C; $\times 10^3$ for H) in Molecule IVa

Atom	x	y	z	Atom	x	y	z
O(1)	155(2)	6389(2)	-1603(2)	C(15)	3069(1)	8648(2)	6748(2)
O(2)	1607(1)	7108(2)	-71(2)	C(16)	2928(2)	9114(2)	5313(2)
O(3)	3769(1)	9168(1)	7988(2)	C(17)	2232(2)	8651(2)	3982(2)
N(1)	-247(1)	9011(1)	3402(2)	C(18)	3914(2)	8720(2)	9473(3)
N(3)	-1397(1)	10113(2)	1589(2)	H(2)	-113(2)	1022(2)	394(3)
N(4)	-1198(1)	9302(1)	-655(2)	H(13)	139(2)	665(2)	560(3)
N(7a)	-257(1)	8748(1)	1955(2)	H(14)	260(2)	742(2)	778(4)
N(9)	642(1)	7046(1)	-603(2)	H(16)	337(2)	972(2)	525(3)
N(10)	925(1)	7258(1)	2687(2)	H(17)	214(2)	894(2)	305(3)
C(2)	937(2)	9829(2)	3079(3)	H(18)	-33(2)	820(2)	-301(4)
C(3a)	974(1)	9411(1)	869(2)	H(28)	-145(2)	774(3)	-319(4)
C(5)	714(1)	8489(2)	-1103(2)	H(38)	-132(2)	903(3)	-331(3)
C(7)	28(1)	7804(1)	-19(2)	H(111)	46(2)	588(2)	159(3)
C(8)	281(1)	7905(1)	1561(2)	H(211)	109(3)	565(3)	334(4)
C(10)	-972(2)	8365(2)	-2797(3)	H(311)	169(2)	596(3)	217(4)
C(11)	1055(2)	6087(2)	2416(3)	H(118)	144(2)	921(3)	1016(4)
C(12)	1647(1)	7729(1)	4070(2)	H(218)	322(2)	878(2)	961(3)
C(13)	1791(2)	7265(2)	5500(2)	H(318)	418(2)	799(2)	956(3)
C(14)	2498(2)	7715(2)	6830(2)				

TABLE 7. Bond Lengths in Molecule IVa

Bond	l, Å	Bond	l, Å	Bond	l, Å
O(1)—N(9)	1,230(3)	N(10)—C(7)	1,356(2)	C(12)—C(13)	1,391(3)
O(2)—N(9)	1,223(3)	N(10)—C(11)	1,470(3)	C(12)—C(17)	1,391(3)
O(3)—C(15)	1,366(2)	N(10)—C(12)	1,435(2)	C(13)—C(14)	1,385(3)
O(3)—C(18)	1,430(3)	C(2)—H(2)	1,04(2)	C(13)—H(13)	0,94(3)
N(1)—N(7a)	1,374(2)	C(5)—C(6)	1,419(2)	C(14)—C(15)	1,389(3)
N(1)—C(2)	1,325(3)	C(5)—C(8)	1,494(3)	C(14)—H(14)	0,91(3)
N(3)—C(2)	1,349(3)	C(6)—C(7)	1,390(2)	C(15)—C(16)	1,397(3)
N(3)—C(3a)	1,328(2)	C(8)—H(18)	0,97(4)	C(16)—C(17)	1,386(3)
N(4)—C(3a)	1,345(2)	C(8)—H(28)	0,98(4)	C(16)—H(16)	0,96(3)
N(4)—C(5)	1,328(2)	C(8)—H(38)	0,98(3)	C(17)—H(17)	0,90(3)
N(7a)—C(3a)	1,389(2)	C(11)—H(111)	0,94(3)	C(18)—H(118)	0,98(3)
N(7a)—C(7)	1,377(2)	C(11)—H(211)	0,99(3)	C(18)—H(218)	0,99(3)
N(9)—C(6)	1,462(3)	C(11)—H(311)	0,97(4)	C(18)—H(318)	0,96(3)

TABLE 8. Bond Angles for Compound IVa

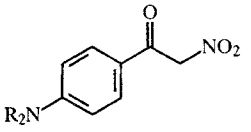
Angle	ω°	Angle	ω°	Angle	ω°
C(15)O(3)C(18)	117,3(2)	N(9)C(6)C(5)	117,4(2)	C(12)C(13)H(13)	121(2)
N(7a)N(1)C(2)	100,6(2)	N(9)C(6)C(7)	118,8(1)	C(14)C(13)H(13)	118(2)
C(2)N(3)C(3a)	102,9(2)	C(5)C(6)C(7)	123,5(2)	C(13)C(14)C(15)	120,0(2)
C(3a)N(4)C(5)	116,4(2)	N(7a)C(7)N(10)	119,0(1)	C(13)C(14)H(14)	122(2)
N(1)N(7a)C(3a)	110,0(1)	N(7a)C(7)C(6)	112,6(1)	C(15)C(14)H(14)	118(2)
N(1)N(7a)C(7)	127,1(1)	N(10)C(7)C(6)	128,2(1)	O(3)C(15)C(14)	124,6(2)
C(3a)N(7a)C(7)	122,7(1)	C(5)C(8)H(18)	109(2)	O(3)C(15)C(16)	116,1(2)
O(1)N(9)O(2)	124,1(2)	C(5)C(8)H(28)	111(2)	C(14)C(15)C(16)	119,2(2)
O(1)N(9)C(6)	117,9(2)	C(5)C(8)H(38)	109(2)	C(15)C(16)C(17)	120,7(2)
O(2)N(9)C(6)	118,0(2)	H(18)C(8)H(28)	106(3)	C(15)C(16)H(16)	119(2)
C(7)N(10)C(11)	121,0(2)	H(18)C(8)H(38)	113(3)	C(17)C(16)H(16)	120(2)
C(7)N(10)C(12)	120,8(1)	H(28)C(8)H(38)	109(3)	C(12)C(17)C(16)	120,0(2)
C(11)N(10)C(12)	117,2(2)	N(10)C(11)H(111)	106(2)	C(12)C(17)H(17)	119(2)
N(1)C(2)N(3)	117,6(2)	N(10)C(11)H(211)	110(2)	C(16)C(17)H(17)	121(2)
N(1)C(2)H(2)	121(1)	N(10)C(11)H(311)	111(2)	O(3)C(18)H(118)	102(2)
N(3)C(2)H(2)	122(1)	H(111)C(11)H(211)	109(3)	O(3)C(18)H(218)	106(2)
N(3)C(3a)N(4)	127,7(2)	H(111)C(11)H(311)	110(3)	O(3)C(18)H(318)	111(2)
N(3)C(3a)N(7a)	108,8(2)	H(211)C(11)H(311)	109(3)	H(118)C(18)H(218)	113(2)
N(4)C(3a)N(7a)	123,5(1)	N(10)C(12)C(13)	121,2(2)	H(118)C(18)H(318)	110(3)
N(4)C(5)C(6)	121,3(2)	N(10)C(12)C(17)	119,6(2)	H(218)C(18)H(318)	114(2)
N(4)C(5)C(8)	116,2(2)	C(13)C(12)C(17)	119,2(2)		
C(6)C(5)C(8)	122,5(2)	C(12)C(13)C(14)	120,9(2)		

Important characteristic of the mass spectra of the arylnitroazolopyrimidines IIa—d are the very high intensity of the singly charged molecular ion peak $[M]^+$ (none of the intensities of the other peaks exceed 15% of that of $[M]^+$) and the presence of peaks corresponding to the doubly charged molecular ion $[M]^{++}$. The ion with maximum intensity for the diethylaminophenyl derivative IIIa is $[M-CH_3]^+$, which is characteristic of compounds containing N—ethyl groups. These results indicate the high thermodynamic stability of the 6—nitro—7—aryltriazolopyrimidine system. The fragmentation pathway is characteristic for nitroazines and this is confirmed by the presence of the ions $[M-NO]^+$, $[M-NO_2]^+$, and also $[M-OH]^+$ (α—elimination, characteristic of *ortho*—substituted nitroarenes). The molecular ion peaks $[M]^+$ are also maximal in the spectra of compounds IVa and b (but relatively less intense), but doubly charged molecular ion peaks, $[M]^{++}$, are absent. The same characteristic ions are formed in the initial stages of fragmentation. In addition peaks were noted which indicate elimination of a methoxy group from the molecular ion.

X—ray structural studies of compounds IIa and IVa (Figs. 1 and 2, Tables 3—8) were carried out to determine the structures of the synthesized series II and IV and to establish and compare their geometric parameters.

Analysis of the bond length distribution shows the geometrically equivalent parameters in the structures of the two compounds are practically identical and that there is a notable alternation of double and single bond lengths in the triazolo[1,5—*a*]pyrimidine unit (the $N_{(1)}$—$C_{(2)}$, $N_{(3)}$—$C_{(3a)}$, $N_{(4)}$—$C_{(3)}$, and $C_{(6)}$—$C_{(7)}$ bonds have the smallest residuals, but they are multiple bonds). This fragment is planar in both molecules. The rotation of the nitro group around the C—N bond is 67.9° and 55.1° in IIa and IVa respectively. The dimethylamino group in IIa is practically coplanar with the benzene ring, the angle between the latter and the $N_{(10)}C_{(13)}C_{(16)}C_{(17)}$ being 3.5°.The angle between the benzene ring and the triazolopyrimidine unit in compound IIa is 52.8°. In IVa the planes of the corresponding fragment makes angles 75.8 and 39.3° with the plane of the benzene ring and the $N_{(10)}C_{(7)}C_{(11)}C_{(12)}$ plane (the interplane angle between the two latter planes is 48.6°).

Variation of the substituents in the triazolopyrimidinones, including use of the arylated compounds Ie and If (R^1 = R^2 = H) as starting materials, gave unexpected results. After decomposition of the residual $POCl_3$ with water and ice, the ω—nitroacetophenones Va and b were isolated. The melting point and physicochemical characteristics of compound Va correspond to those reported previously [7].



Va, b

V a R = Me; b R = Et

In explaining the formation of these unexpected reaction products one can only assume that the reaction described above for the *p*—substituted compound occurs initially to give compounds of series II or III, and the latter are then decomposed by water to give the acetophenones Va and Vb.

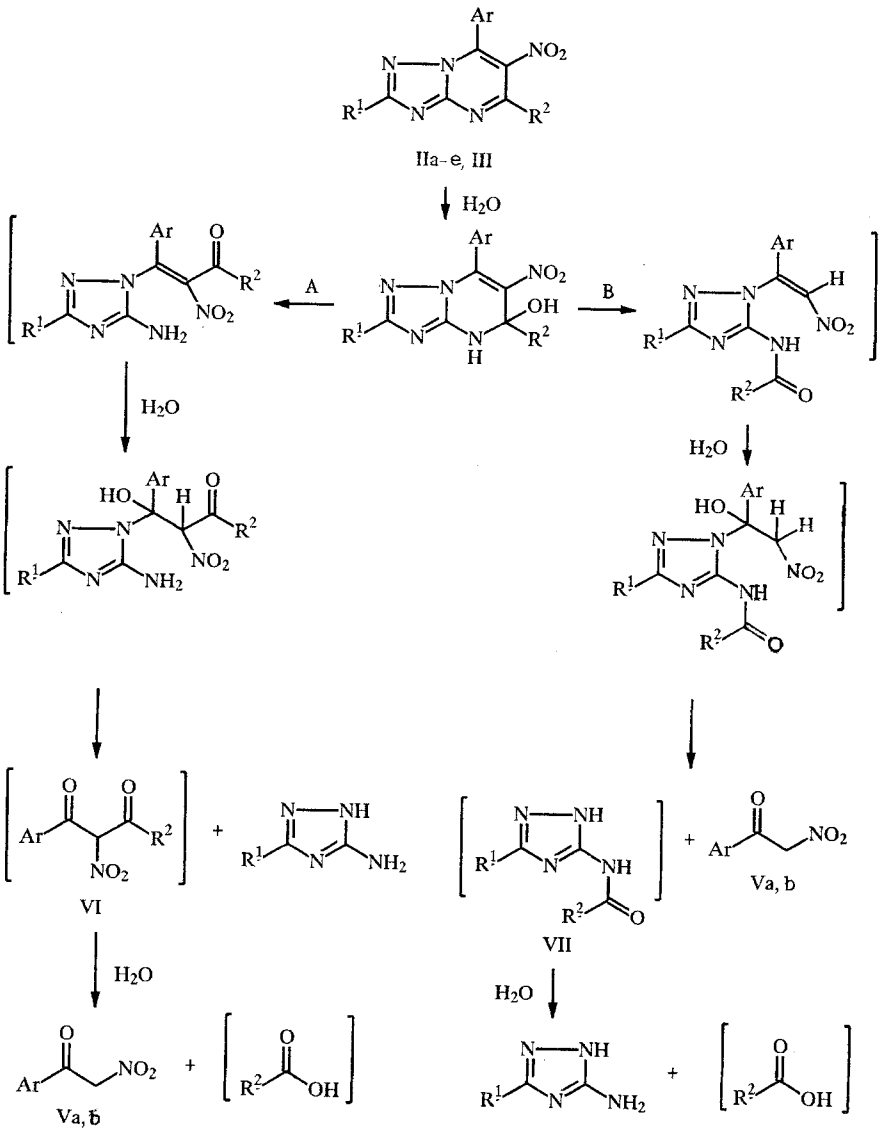
To confirm this suggestion we carried out the reaction with 2—phenyl—6—nitro—7—(*p*—N,N—dimethylaminophenyl)—1,2,4—triazolo[1,5—*a*]pyrimidine (IId) (Table 1) which is easily isolated because of its very low solubility in water. After adding water to an ethanolic solution of compound IId and prolonged boiling of the mixture, the nitroacetophenone Va and 3—amino—5—phenyl—1,2,4—triazole were isolated from the reaction mixture.

A destruction of the pyrimidine ring with elimination of the two carbon fragment $C_{(4)}$—$C_{(5)}$ was previously unknown so we studied the reaction more closely.

Compounds Ia—d with a methyl substituent in the azine ring underwent the same decomposition under more stringent conditions, namely heating in aqueous ethanolic NaOH solution (pH 11—12), than needed for R^2 = H. The same acetophenones, Va and b, were obtained.

The greater stability of the 5—methylazolopyrimidines relative to the 5H derivative may be explained by steric factors and also by the greater electrophilicity of the bond between $C_{(5)}$ and hydrogen in compounds IId—f in comparison with the corresponding carbon atom arylazolopyrimidines IIa—c which are bonded to methyl groups. It should be noted that the azole substituent R^1 does affect the course of the reaction but to a lesser extent. For example, a strongly electron withdrawing substituent at this position (R^1 = CF_3) facilitates decomposition.

Starting from these observations, two possible reaction mechanisms, A and B, each involving at least three molecules of water, can be postulated:



We believe that scheme A is the more likely. The susceptibility of the pyrimidine system to decomposition by nucleophiles, including rupture of the N(1)—C(6) and N(3)—C(4) bonds to give compounds containing the C(4)—C(5)—C(6) fragment [8] supports this view. It is also known that β—diketones (compound VI, scheme A) may be split to give ketones [9]. The fact that, as we have established, 3—acetylamino—1,2,4—triazole (compound VII, scheme B) is not hydrolyzed under the reaction conditions to an amine serves as confirmation that the $N_{(4)}$—$C_{(5)}$ bond breakage occurs first (mechanism A) rather than $C_{(5)}$—$C_{(6)}$ bond breakage (mechanism B).

EXPERIMENTAL

X-Ray Crystallographic Analysis of the Nitrotriazolopyrimidines IIa and IVa. Crystals of compound IIa are triclinic and crystallize as the hemihydrate, = 6.204(2), b = 11.038(3), c = 12.784(4) Å, α = 74.58(2), β = 75.78(2), γ = 82.22(2)°, V = 815.8(4) Å^3, Z = 2, $C_{14}H_{14}N_6O_2 \cdot \frac{1}{2}H_2O$, space group P$\bar{1}$. Crystals of compound IVa are monoclinic, a 13.458(6), b = 12.191(5), c = 9.265(4) Å, β = 110.12(3)°, V = 1426(1) Å^3, Z = 4, $C_{14}H_{14}N_6O_3$, space group P 2_1/n. Both structures were solved by direct methods and refined full matrix least squares in the anisotropic approximation (in structure IVa the hydrogen atoms were found from difference syntheses and were refined isotropically; the hydrogen atoms were not

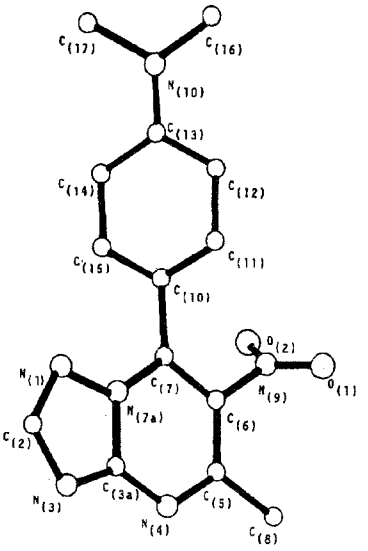


Fig. 1. Structure of the molecule of compound IIa.

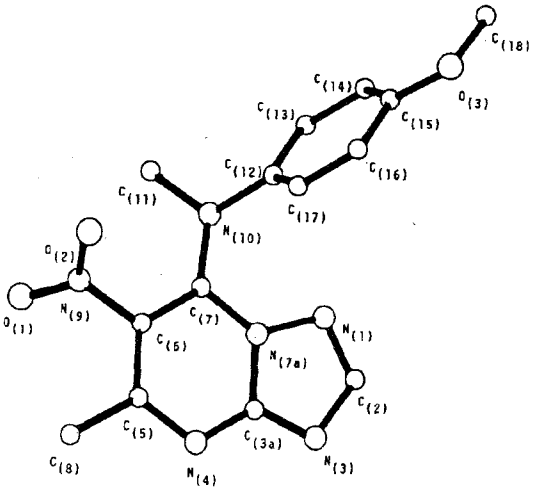


Fig. 2. Structure of the Molecule of Compound IVa.

found in IIa because the crystal decomposed during data collection) to $R = 0.095$ ($R_w = 0.097$) and $R = 0.053$ ($R_w = 0.065$) for 1350 and 2425 reflexions for IIa and IVa respectively. Intensity data were collected with a Syntex P1 diffractometer, graphite monochromator, $\theta/2\theta$ scanning with $3 \leq 2\theta \leq 53°$.

IR spectra were recorded in nujol with UR—20 spectrometer. ^{1}H NMR spectra were obtained in DMSO—D_6 with TMS as internal standard on a Bruker WP—80 spectrometer. Mass spectra were recorded with a Varian MAT-311A instrument.

Results of C, H, and N elemental analysis agreed with calculated values.

6—Nitro—7—(*p*—N,N—dialkylaminophenyl—1,2,4—triazolo[1,5—*a*]pyrimidines IIa—d, and IIIa, and 6—nitro—7—(N—methyl—*p*—methoxyphenylamino)—1,2,4—triazolo[1,5—*a*]pyrimidines IVa and IVb, and ω—nitroacetophenones Va and Vb (General method). A mixture of compounds Ia—e (0.025 mol) and an N,N—dialkylaniline or N,N—dimethyl—*p*—anisidine (0.05 mol) was boiled for 2 h with $POCl_3$ (0.3 mol), the excess $POCl_3$ was distilled away, and the reaction mass was mixed with water and ice (150 ml), and extracted twice with chloroform (compound IId precipitated from the aqueous solution), and the product was recrystallized from ethanol after evaporation of the chloroform to give 4—N,N—dimethylamino—ω—nitroacetophenone (Va, $C_{10}H_{12}N_2O_3$), yield 67%, m.p. 170—171° C. IR spectrum: 1680 cm^{-1} (C=O), ^{1}H NMR spectrum: 3.09 (6H, s, $N(CH_3)_2$), 6.20 (2H, s, CH_2), 6.68 (2H, d, 3′,5″—H), 7.69 ppm (2H, d, 2′,6′—H). Mass spectrum (*m/z* (I, %); 208 (97, M^+), 148 (50), 134 (100).

4,4—N,N—diethylamino—ω—nitroacetophenone (Vb, $C_{12}H_{16}N_2O_3$). Yield 63%, m.p. 115—117° C. IR spectrum: 1670 cm^{-1} (C=O). ^1H NMR spectrum: 1.13 (6H, t, NCH_2H_3), 3,45 (4H, q, NCH_2CH_3), 6.29 (2H, s , CH_2), 6.71 (2H, d, 3′,5′—H), 8.68 ppm (2H, d, 2′,6′—H). Mass spectrum (*m/z* (I,%)): 236 (100, M^+), 221 (92), 176 (59), 162 (95).

REFERENCES

1. V. P. Rusinov, A. A. Tumashov, E. O. Sidorov, I. V. Karpin, and O. N. Chupakhin, Zh. Org. Khim., (in press).
2. Weigand—Hilgetag. Experimental Methods in Organic Chemistry [Russian translation], Khimiya, Moscow (1969), p. 229.
3. E. Lippman, U. Hempel, E. Tenor, and E. Thomas, East German Pat. 255 735A1, Ref. Zh. Khim., 6H1232P (1989).
4. V. P. Rusinov, M. N. Kushnir, and O. N. Chupakhin, Abstr. Sixth European Symposium on Organic Chemistry, Belgrade (1989), p. 251.
5. E. Lippman, U. Hempel, and E. Tenor, Z. Chem., **170**, No. 5 (1990).
6. V. A. Koptyug, Arenonium Ions [in Russian], Nauka, Novosibirsk (1991).
7. M. A. Ashwell and R. F. W. Jackson, Synthesis, No. 3, 229 (1988).
8. V. P. Rusinov and A. N. Chupakhin, Nitroazines [in Russian], Nauka, Novosibirsk (1991).
9. J. March. Organic Chemistry [Russian translation], Mir, Moscow (1987), Vol. 2, p. 474.