2-Propionyl-5-tert-butyl-N,N,O-azoxybenzene (II) gave 1.29 g (32%) of 2,2'-dimethyl-6,6'-di-tert-butyl-2,2'-diindoxyl (VII)* and 0.57 g (29%) of azoxybenzene (VI).

The reaction of 2-propionyl-5-bromo-N,N,O-azoxybenzene (III) in methanol gave 1.38 g (27%) of 2-methyl-2-methoxy-6-bromoindolinone (VIII)* and 0.47 g (24%) of azoxybenzene (VI).

The reaction of III in ethanol gave 1.30 g (24%) of 2-methyl-2-ethoxy-6-bromoindolinone (IX)* and 0.43 g (22%) of azoxybenzene (VI).

The reaction of 2-propionyl-4'-acetyl-N,N,O-azoxybenzene (X) gave 0.64 g (22%) of 2,2'-dimethyl-2,2'-diindoxyl (V) and 0.68 g (24%) of 4,4'-diacetylazoxybenzene (XII).*

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REACTIONS OF HETEROCYCLIC CATIONS WITH N-CONTAINING NUCLEOPHILES. 13.* INVESTIGATION OF THE REACTION OF 2,4,6-TRIARYLPYRYLIUM SALTS WITH HYDRAZINES, SEMICARBAZIDE, AND THIOSEMICARBAZIDE

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The recyclization reactions of 2,4,6-triphenylpyrylium perchlorate with hydrazine and methyl-, phenyl-, benzoyl-, and benzalhydrazines in dimethylformamide (DMF), which proceed differently than in ethanol, were examined. 7-Oxo and 7-thioxo derivatives of 2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine were obtained by transformation of 2,4,6-triarylpyrylium salts with semicarbazide and thiosemicarbazide in DMF. The tautomeric forms of the products were established by mass spectrometry and chemical transformations.

It is known that 2,4,6-triarylpyrylium perchlorates (I) react with hydrazine in ethanol to give 4H-1,2-diazepines (II) [2-4]. Under the same conditions 2,4,6-triphenylpyrylium perchlorate (a) reacts with methylhydrazine to give primarily 1-methyl-3,5-diphenylpyrazole [5] and with phenylhydrazine to give 3,5-diphenyl-5-phenacyl-2-pyrazoline [2].

We have shown that the direction of these reactions can be changed if they are carried out in dimethylformamide (DMF). Thus the principal reaction product is 3,5-diphenylpyrazole (IIIa) when salt Ia is refluxed with hydrazine in DMF. Similarly, under the same conditions the reaction of salt Ia with phenylhydrazine leads to 1,3,5-triphenylpyrazole (IIIb). The previously described pyrazolo[2,3-a]quinoline (IV) [6] is formed simultaneously by intramolecular cyclization of the intermediate 1,3,5-triphenyl-5-phenacylpyrazoline. The recyclization of perchlorate Ia with methylhydrazine in DMF proceeds differently with the formation of 1-methylamino-substituted pyridinium salt V. 2,4,6-Triphenylpyridine (VIa) is isolated simultaneously, probably as a consequence of partial thermal destruction of salt V or methylhydrazine with the formation of ammonia.

*See [1] for Communication 12.
†Deceased.

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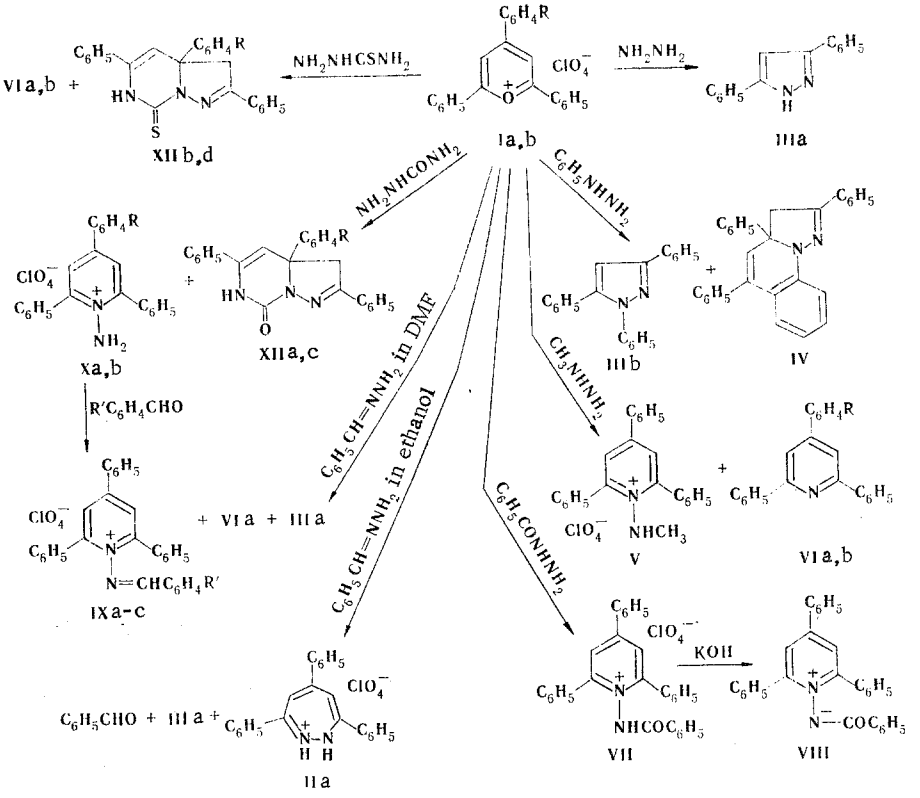
It is known that perchlorate Ia forms pentene-1,5-dione monobenzoylhydrazone upon brief refluxing in DMF with excess benzoylhydrazine [7]. We have found that these reagents form 1-benzamidopyridinium salt VII under the same conditions but at a reagent ratio of 1:1.2. Salt VII was also obtained when the reaction was carried out in ethanol [8]. Since perchlorate VII has been described with a different melting point [8], it was converted to betaine VIII by the action of potassium hydroxide in order to prove its structure.

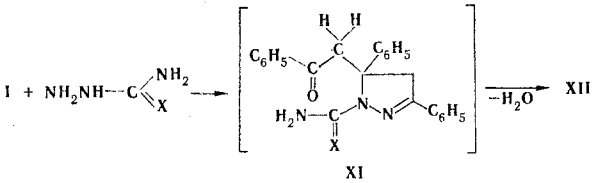
We also studied the reaction of salt Ia with benzalhydrazine. The pyrylium cation undergoes recyclization to pyrazole IIIa in DMF. Small amounts of pyridine VIa and 1-benzylideneaminopyridinium perchlorate IXa are also formed simultaneously. Salt IXa was obtained by alternative synthesis by the reaction of 1-amino-2,4,6-triphenylpyridinium perchlorate (Xa) with benzaldehyde. The reaction of benzalhydrazine with salt Ia in ethanol leads to 3,5,7-triphenyl-1,2-diazepinium perchlorate (IIa), benzaldehyde, and pyrazole IIIa. Thus one can obtain five-, six-, and seven-membered nitrogen heterocycles in the reaction of salt Ia with benzalhydrazine by changing the solvent.

We demonstrated that the reaction of perchlorate Ia with semi- and thiosemicarbazides in DMF also proceeds differently than in ethanol [9, 10].



I, VI, X a R = H; b R = *p*-OCH_3; IXa R′ = H; b R′ = *p*-$(CH_3)_2N$; c R′ = *p*-NO_2; XIIa,b R = H; c,d R = *p*-OCH_3

It might be assumed that, as in the reaction with phenylhydrazine in ethanol [2], N-substituted 5-phenacyl-2-pyrazoline (XI) is formed initially. Subsequent intramolecular condensation of the amino group of the substituent with the phenacyl carbonyl group results in the formation of the 3H-pyrazolo[1,5-c]pyrimidine (XIII) condensed heterocyclic system:



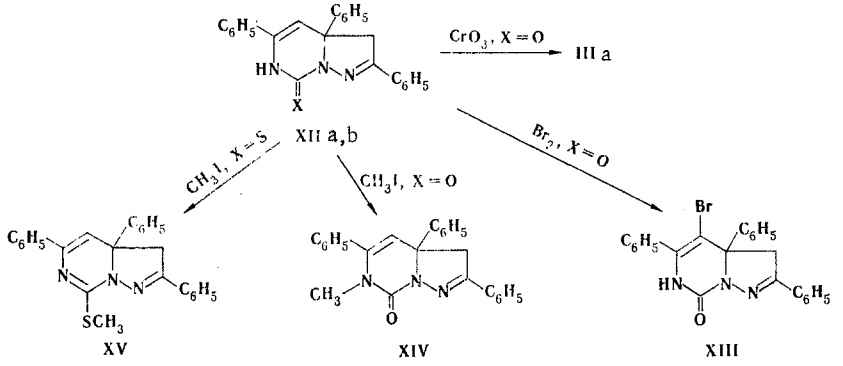
In addition to this process, one observes, just as in ethanol, the formation of the corresponding pyridinium salts, which under the reaction conditions undergo cleavage to pyridine VIa (reaction with thiosemicarbazide) or 1-aminopyridinium salt Xa (reaction with semicarbazide). Salt Xa reacts with aromatic aldehydes to give azomethines IX. Pyrazolo-

[1,5-c]pyrimidines XIIc,d were also obtained in the reactions of perchlorate Ib with semicarbazide and thiosemicarbazide.

The IR spectra of XII in chloroform contain bands of stretching vibrations of an associated NH group (3170, 3200 cm^{-1}), heteroring C=C and C=N bonds (1600-1610 cm^{-1}), the CO group in XIIa,c (1670 cm^{-1}), and the C=S group in XIIb,d (1250-1255, 1270-1280 cm^{-1}). The PMR spectrum of XIIa contains singlets at 3.6 (2H, 3-CH_2) and 5.9 ppm (1H, pyrimidine ring). Similarly, the PMR spectrum of XIIb contains singlets at 3.7 (CH_2) and 5.9 ppm (CH), which remain unchanged after deuteration.

To confirm the structure of XII we studied some of their transformations. Thus oxidation of XIIa with chromium trioxide leads to destruction of the pyrimidine ring, and 3,5-diphenylpyrazole (IIIa) is isolated from the reaction.

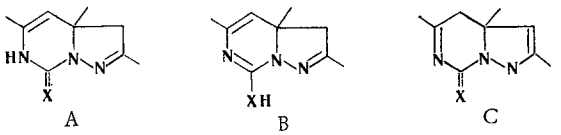
Bromination of the double bonds is not observed in the bromination of XIIa with 1 mole of bromine in ethanol–pyridine solution; instead, one observes the characteristic (for pyrimidines [12]) substitution to give monobromo derivative XIII. The bromine atom is in the 4 position of the starting heterocycle, since the peak of the CH group at 5.9 ppm vanishes in the PMR spectrum of XIII. The protons of the CH_2 group show up in the form of an AB spectrum (3.55 and 3.98 ppm, J_{AB} = 16.0 Hz).



It must be noted that the pyrazolo[1,5-c]pyrimidine heteroaromatic system has been described in the literature [13, 14]. However, we were unable to detach the phenyl substituent from the 3a position in XIIa,b by chemical methods in order to achieve heteroaromatization.

In addition to the molecular-ion peaks, characteristic peaks of fragment ions (Table 1), among which the most intense peak belongs to the $[M - C_6H_5]^+$ ion, are present in the mass spectra of XIIa,b. It is apparent from Table 1 that both compounds fit into the overall fragmentation scheme.

Taking into account the data from the PMR spectra, three tautomeric forms (A, B, or C) can be proposed for XII:



The presence of absorption bands of C=O and C=S groups in the IR spectra makes it possible to exclude structure B for XIIa,b. The solution of the problem as to the tautomeric form (A or C) in which these compounds exist was found by a study of the UV spectra of their fixed forms. For this, we methylated the indicated substances and obtained XIV and XV. The absorption band of a carbonyl group (1660 cm^{-1}) is retained in the IR spectrum of XIV in chloroform. The appearance in the mass spectrum of this compound of peaks of $[M - C_6H_5CNCH_3]^+$ (m/z 261), $C_6H_5\overset{+}{C}NCH_3$ (m/z 118), and $[M - CONCH_3]^+$ (m/z 322) ions (Table 2) indicates that methylation took place at the nitrogen atom adjacent to the carbonyl group. Thus XIV exists in the A form. Absorption bands of a C=S group are absent in the IR spectrum of XV. A peak with m/z 348 (Table 2), which corresponds to the elimination of an SCH_3 group from the molec-

TABLE 1. Data on the Mass-Spectrometric Fragmentation of XIIa,b

Fragment ions, X = O (XIIa) and S (XIIb)	m/z values	
	XIIa	XIIb
$M^{+\cdot}$	365	381
$[M-CXNH]^+$	322	322
$[M-C_6H_5]^+$	288	304
$[M-C_6H_5CN]^{+\cdot}$	262	278
$[M-C_6H_5CNH]^+$	261	277
$[(M-C_6H_5)-CXNH]^+$	245	245
$C_6H_5^+$	77	77

TABLE 2. Data on the Mass-Spectrometric Fragmentation of XIV and XV

Fragment ions	m/z values	
	XIV	XV
$M^{+\cdot}$	379	395
$[M-CH_3]^+$	—	380
$[M-SCH_3]^+$	—	348
$[M-CONCH_3]^+$	322	—
$[M-C_6H_5]^+$	302	318
$[M-C_6H_5CN]^{+\cdot}$	276	292
$[M-C_6H_5CNCH_3]^+$	261	—
$[M-CONCH_3-C_6H_5]^+$	245	—
$[M-CNSCH_3-C_6H_5]^+$	—	245
$C_6H_5-C\equiv N^+-CH_3$	118	—
$(C_6H_5-C\equiv N)^{+\cdot}$	103	103
$C_6H_5^+$	77	77

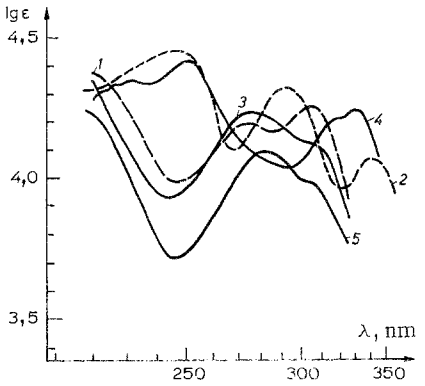


Fig. 1. UV spectra: 1) 7-hydroxy-6-methyl-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XIV); 2) 7-methylthio-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XV); 3) 7-hydroxy-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XIIa); 4) 7-thio-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XIIb); 5) 7-hydroxy-4-bromo-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XIII).

lar ion, which is in agreement with the IR spectroscopic data and indicates that XV exists in the B form, is observed in its mass spectrum. The CH_2 group in both compounds is located in the pyrazoline ring. These conclusions are also confirmed by data from the PMR spectra of XIV [2.8 (s, 6-CH_3), 3.5 (s, 3-CH_2), and 5.6 ppm (s, 4-CH); intensity ratio 3:2:1] and XV [2.6 (s, SCH_3), 3.5 (s, 3-CH_2), and 6.1 ppm (s, 4-CH); intensity ratio 3:2:1].

A comparison of the UV spectra of XIIa and XIV shows good agreement between the absorption maxima and indicates that XIIa also exists in the A form. On the other hand, the difference in the absorption maxima in the UV spectra of XIIb and XV confirms the IR spectroscopic data, which indicate that the hydrogen atom in pyrazolopyrimidine XIIb is bonded to the nitrogen rather than the sulfur atom. In analogy with XIIa, it may be assumed that this hydrogen atom is bonded to the nitrogen atom of the pyrimidine ring and that XIIb also exists in the A form in the investigated solvents.

Data from the UV spectrum of XIII make it possible to assume that it also exists in the A form.

EXPERIMENTAL

The IR spectra of mineral oil suspensions and chloroform solutions of the compounds were recorded with a Specord 71-IR spectrometer. The UV spectra of solutions in isopropyl alcohol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions

in chloroform were recorded with a Tesla BS-467C spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with a Varian MAT-112 spectrometer at an ionizing-electron energy of 70 eV and an ionization-chamber temperature of 180°C with direct introduction of the samples into the ion source. The purity of the compounds obtained was monitored by means of thin-layer chromatography (TLC) on aluminum oxide in heptane–ethyl acetate (9:1), chloroform, or benzene and on silicic acid in chloroform (perchlorates IIa and V). Data on the synthesized compounds are presented in Table 3.

Reaction of Salt Ia with Hydrazine Hydrate. The reaction was carried out by refluxing the indicated components in a ratio of 1:1.5 in dry DMF for 30 min (the hydrazine hydrate was added to a hot solution of perchlorate Ia in DMF), after which the reaction mixture was cooled and treated with ether, and the ether solution layer was separated and washed with water. The ether was removed by distillation, and the residue was recrystallized from toluene to give pyrazole IIIa, with mp 198-199°C (mp 199°C [4]), in 85% yield.

Reaction of Perchlorate Ia with Methylhydrazine. A mixture of methylhydrazine sulfate, fused potassium acetate, and salt Ia in a ratio of 1.2:1.2:1 was refluxed with stirring in dry DMF for 30 min, after which it was cooled, and ether was added. The liberated oil was reprecipitated from acetone by the addition of water to give pale-yellow 1-methylamino-2,4,6-triphenylpyridinium perchlorate in 47% yield. The ether solution was washed with water and dried, the solvent was evaporated, and the residue was separated with a chromatographic column filled with aluminum oxide by elution with benzene to give pyridine VIa, with mp 137-138°C, in 22% yield. The product was identical to the previously obtained compound.

Reaction of Salt Ia with Phenylhydrazine. This reaction was carried out in the same way as the reaction with hydrazine hydrate but at a ratio of 1:1.2. A small amount of benzene was added to the residue after removal of the ether by distillation, and the undissolved pyrazolo[2,3-a]quinoline IV (35%), with mp 193-194°C (from cyclohexane), was removed by titration; no melting-point depression was observed for a mixture of this product with the compound obtained by the method in [6]. Pyrazole IIIb was precipitated from the benzene filtrate by means of petroleum ether and dissolved in ether–acetic acid. The solution was treated with 70% $HClO_4$, and the 1,3,5-triphenylpyrazole perchlorate (50%), with mp 244-245°C (from acetic acid) (mp 245°C [2]), was removed by filtration. Found: C 63.3; H 4.2; Cl 8.9%. $C_{21}H_{17}ClN_2O_4$. Calculated: C 63.5; H 4.3; Cl 8.9%.

1-Benzamido-2,4,6-triphenylpyridinium Perchlorate (VII). This compound was obtained by reaction of salt Ia with benzoylhydrazine by a similar method. Salt VII was precipitated from the reaction mixture by means of ether.

1-(2,4,6-Triphenylpyridinia)benzoylimine (VIII). This compound was formed by mixing equimolar amounts of salt VII and KOH in methanol. After 30 min, the $KClO_4$ was removed by filtration, and the solvent was evaporated from the filtrate.

Reaction of Perchlorate Ia with Benzalhydrazine. A) The indicated compounds in a ratio of 1:1.2 were refluxed in absolute ethanol for 1 h, after which the mixture was cooled and treated with ether, and perchlorate IIa was removed by filtration. The filtrate was washed with water, the ether was removed by distillation, and the residue was separated with a chromatographic column filled with aluminum oxide by elution with benzene. The principal fraction contained pyrazole IIIa, which was obtained in 48% yield.

B) The same components in ratio of 1:1.2 were refluxed for 30 min in DMF, after which the mixture was treated with ether to give an oil, which solidified after reprecipitation from acetone by means of water. This procedure gave 1-benzylideneamino-2,4,6-triphenylpyridinium perchlorate (IXa) in 10% yield. The ether layer was worked up as in method A, and pyrazole IIIa (70%) and pyridine VIa (10%) were isolated by chromatography or by fractional crystallization.

Perchlorate IXa was also obtained by refluxing salt Xa with benzaldehyde in glacial acetic acid for 2 h. The reaction mixture was cooled, and the precipitate was removed by filtration. Perchlorates IXb,c were similarly obtained, but the reaction mixtures were refluxed for 30 min and 1.5 h, respectively, and the substances were precipitated from the reaction mixtures by means of ether.

7-Oxo-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XIIa). A mixture of 4.08 g (10 mmole) of perchlorate Ia, 1.34 g (12 mmole) of semicarbazide hydrochloride, and 1.20 g (12 mmole) of fused potassium acetate was refluxed in 7 ml of DMF for 30 min, after which it was cooled, and the precipitate was removed by filtration and washed with a small amount

TABLE 3. Characteristics of the Synthesized Compounds

Compound	mp,[a] °C	IR spectrum, cm^{-1}	Found, %				Empirical formula	Calc., %				Yield, %
			C	H	Cl	N		C	H	Cl	N	
IIa	211	1610, 1580, 1560, 1490, 1365, 1095	65,3	4,4	8,5	6,3	$C_{23}H_{19}ClN_2O_4$	65,3	4,5	8,4	6,6	48
V	182—183	3340, 1630, 1600, 1570, 1100	65,8	5,0	8,3	6,5	$C_{24}H_{21}ClN_2O_4$	66,0	4,8	8,1	6,4	47
VII	246,5[b]	3345, 1695, 1620, 1600, 1575, 1125	68,0	4,7	6,7	5,1	$C_{30}H_{23}ClN_2O_5$	68,4	4,4	6,7	5,3	80
VIII	211[c]	1610, 1585, 1550, 1350	84,3	5,0	—	6,6	$C_{30}H_{22}N_2O$	84,5	5,2	—	6,6	85
IXa	239—240	1625, 1605, 1570, 1095	70,6	4,7	7,3	—	$C_{30}H_{23}ClN_2O_4$	70,5	4,5	6,9	—	61
IXb	132—133	1625, 1590, 1560, 1540, 1110	69,2	5,2	6,8	—	$C_{32}H_{28}ClN_3O_4$	69,4	5,1	6,4	—	90
IXc	232—234	1630, 1600, 1570, 1540, 1350, 1105	64,6	3,8	6,8	—	$C_{36}H_{22}ClN_3O_6$	64,8	4,0	6,4	—	61
Xb	104—105	1627, 1600, 1570, 1470, 1260, 1200, 1110	63,6	4,8	7,6	6,3	$C_{24}H_{21}ClN_2O_5$	63,7	4,7	7,8	6,2	18
XIIa	263—264	3170, 1670, 1600, 1565, 1420	79,0	5,5	—	11,7	$C_{24}H_{19}N_3O$	78,9	5,2	—	11,5	53
XIIb	250—251	3200, 1610, 1530, 1430, 1280, 1250	75,2	5,3	8,1[d]	11,1	$C_{24}H_{19}N_3S$	75,5	5,0	8,4[d]	11,0	40
XIIc	241	3245, 1670, 1640, 1600, 1510, 1420	75,6	5,8	—	10,5	$C_{25}H_{21}N_3O_2$	75,9	5,4	—	10,6	59
XIId	210—211	3125, 1610, 1530, 1500, 1445, 1270, 1255, 1200	73,4	5,4	7,6[d]	10,1	$C_{25}H_{21}N_3OS$	73,0	5,1	7,8[d]	10,2	60
XIII	184	3170, 1680, 1605, 1570, 1420	64,9	4,1	18,4[e]	9,7	$C_{24}H_{18}BrN_3O$	64,9	4,1	18,0[e]	9,5	86
XIV	194—195	1650, 1600, 1485, 1440, 1390	78,9	5,5	—	11,5	$C_{25}H_{21}N_3O$	79,1	5,6	—	11,0	84
XV	163,5—164	1600, 1520, 1455, 1420, 1350	75,6	5,4	7,7[d]	10,5	$C_{25}H_{21}N_3S$	75,9	5,4	8,1[d]	10,6	69

[a]The compounds were recrystallized: IIa, IXa, and XIV from acetic acid, V and VII from ethanol, VIII from toluene, IXb from acetone, IXc from acetic acid—ethanol, Xb from methanol, XIIa from DMSO, XIIb from ethanol—benzene (5:1), XIIc,d from chloroform—petroleum ether, XIII from isobutanol, and XV from benzene. [b]According to [8], this compound had mp 128°C. [c]According to [8], this compound had mp 204°C. [d]Analysis for S. [e]Analysis for Br.

of acetone and a large amount of water to give 1.94 g (53%) of XIIa. Found: M 365. Calculated: M 365.4. Treatment of the filtrate with ether gave a viscous oil, which was reprecipitated from acetone by means of ether and from acetone by means of water to give 1.55 g (37%) of perchlorate Xa with mp 161-163°C (from methanol). The product was identical to the compound obtained in [9].

7-Thioxo-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XIIb). This compound was similarly obtained in the reaction of salt Ia with thiosemicarbazide for 1 h. The reaction mixture was cooled and treated with ether, and the resulting oil was allowed to solidify. The solid was removed by filtration and washed on the filter with ethanol, water, and ether to give XIIb. The ether solution was washed with water and evaporated to give pyridine VIa in 46% yield.

7-Oxo-2,5-3a-(4-methoxyphenyl)-3H-pyrazolo[1,5-c]pyrimidine (XIIc). This compound was similarly obtained from perchlorate Ib and semicarbazide. The oil that was liberated by treatment of the reaction mixture with ether was reprecipitated from acetone by means of water, removed by filtration, dissolved in chloroform, and purified with a chromatographic column filled with aluminum oxide by elution with chloroform. The principal fraction contained XIIc. PMR spectrum: 3.5 (s, 2H, 3-CH_2), 3.6 (s, 3H, O—CH_3), and 5.8 ppm (s, 1H, 4-CH). Perchlorate Xb was eluted from the column by means of acetone.

7-Thioxo-2,5-diphenyl-3a-(4-methoxyphenyl)-3H-pyrazolo[1,5-c]pyrimidine (XIId). This compound was obtained in the same way as XIIc, but the mixture was refluxed for 40 min, after which it was diluted with water, and the product was extracted with ether. The ether was removed by distillation, and the residue was separated with a column as in the preceding method. The first fraction contained pyridine VIb (10%) with mp 98-99°C (from ethanol) (mp 99-100°C [11]). Evaporation of the solvent from the principal fraction gave XIId. PMR spectrum: 3.6 (s, 5H, O—CH_3 and 3-CH_2) and 5.9 ppm (s, 1H, 4-CH).

Oxidation of XIIa. Oxidation was carried out with a fourfold amount of CrO_3 in 90% acetic acid. The mixture was refluxed for 2 h and allowed to stand at room temperature for 2 h. Ether was then added, and the mixture was filtered. The filtrate was washed with water, the ether solution was concentrated, and the precipitate was removed by filtration to give 3,5-diphenylpyrazole, with mp 199°C, in 37% yield. No melting-point depression was observed for a mixture of this product with a genuine sample.

4-Bromo-7-oxo-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XIII). A mixture of 1.14 g (4 mmole) of XIIa and 0.65 g (4.0 mmole) of bromine was refluxed in a mixture of 10 ml of ethanol and 1 ml of pyridine, after which it was cooled, and the precipitate was removed by filtration, washed with water, recrystallized, and dried in vacuo over P_2O_5 at 100°C for 4 h.

7-Oxo-6-methyl-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XIV). A 0.92-g (2.5 mmole) sample of XIIa and 0.13 g (3.15 mmole) of sodium amide were heated in absolute p-xylene for 30 min, after which the mixture was cooled to room temperature and treated with 0.45 g (3.15 mmole) of methyl iodide. The mixture was heated at 40°C for 1 h, at 60°C for 2 h, and at 80°C for 1 h, after which it was cooled, and the precipitate was removed by filtration and washed thoroughly with water to give 0.8 g of XIV.

7-Methylthio-2,3a,5-triphenyl-3H-pyrazolo[1,5-c]pyrimidine (XV). A) This compound was obtained as in the preceding method by methylation of XIIb. The NaI was removed from the reaction mixture by filtration, and the filtrate was concentrated and diluted with petroleum ether to give XV in 69% yield.

B) Equimolar amounts of XIIb and NaOH were heated in DMSO for 15 min, after which the temperature of the reaction mixture was lowered to 30°C, and methyl iodide was added dropwise. The mixture was heated at 70°C for 1.5 h, cooled, diluted with water, and extracted with ether. The ether was removed by distillation, and XV was obtained in the residue in 63% yield.

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sym-TRIAZINE DERIVATIVES. 5.* CONVERSION OF 2,4,6-TRIETHOXYCARBONYL-1,3,5-TRIAZINE TO 2-ETHOXYCARBONYL-4-ARYLHYDRAZINO-5-OXOIMIDAZOLES

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The reaction of 2,4,6-triethoxycarbonyl-1,3,5-triazine with arylhydrazines proceeds with rearrangement and leads to the formation of 2-ethoxycarbonyl-4-arylhydrazino-5-oxoimidazoles. The factors that limit the possibility of the occurrence of the reaction are examined from the point of view of the postulated mechanism.

Together with G. M. Vakhatova, we have previously shown [2] that the reaction of 2,4,6-triethoxycarbonyl-1,3,5-triazine (I) with phenylhydrazine (IIa) takes place at the C=N bonds of the heterocyclic system and is accompanied by rearrangement with the formation of 5-oxoimidazole derivative IIIa.

It seemed of interest to determine the limits of this new rearrangement and to evaluate how the structure of the hydrazine component affects the ease with which it occurs. For this we investigated the reaction with ester I of 2- [3] 3- [4] and 4-methyl- [3], 4-chloro- [3], 4-nitro- [5], and 2,4-dinitrophenylhydrazines (IIb-g), as well as hydrazobenzene. In all cases the process was carried out by refluxing triester I with arylhydrazine II in absolute ethanol with monitoring of the course of the reaction by thin-layer chromatography (TLC) on Silufol UV-254.

We found that the introduction of both electron-donor and electron-acceptor substituents in the para position of phenylhydrazine has no effect on the course of the rearrangement. The yields of oxoimidazole derivatives IIId,f were 75 and 78%. In the case of 4-chlorophenylhydrazine (IIe) the yield of IIIe reached 94%. The yields decreased somewhat (to 53% in the case of IIb and to 62% in the case of IIc) on passing from the p- to the m- and o-methyl-substituted compounds.

*See [1] for Communication 4.

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