1,3,4-OXADIAZOLO[3,2-*a*]PYRIMIDINIUM SALTS

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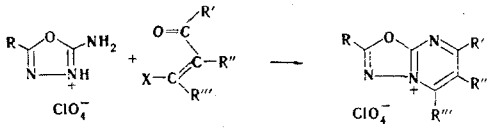
5-Amino-1,3,4-oxadiazolium perchlorates react with 1,3-carbonyl-functional compounds to give 1,3,4-oxadiazolo[3,2-*a*]pyrimidinium perchlorates. The latter are cleaved by both alkali and strong acid to give 1-amino-2-pyrimidinone or 5-amino-1,3,4-oxadiazole derivatives. The 1,3,4-oxadiazolo[3,2-*a*]pyrimidinium perchlorates react with anailine and hydrazines to give sym-triazolo[1,5-*a*]pyrimidinium salts and with acetylacetone to give pyrazolo[1,5-*a*]pyrimidines.

As we have previously shown [1], protonated 5-amino-1,3,4-oxadiazoles I react with β-diketones to give the previously unknown 1,3,4-oxadiazolo[3,2-*a*]pyrimidinium salts (II). Methods for the synthesis of derivatives of this new heterocyclic cation and some of their transformations are described in greater detail below.

Not only β-diketones but also β-keto aldehydes and their acetals, β-chlorovinyl ketones, β-chlorovinyl aldehydes, and malonaldehyde acetals react with I to give salts II (see Table 1).



I II

Like other condensed pyrimidinium compounds [2], salts II give polymethine dyes at both methyl groups (the 5-methyl group is more reactive). Dyes – mono- (at 5-CH_3) and distyryls – were obtained from IIc and p-dimethylaminobenzaldehyde. The structure of the monostyryl is confirmed by its PMR spectrum, in which the signal of the 5-CH_3 group vanishes and the signal of the 7-CH_3 group remains.

In the PMR spectra of II, the signal of the 5-CH_3 group is always lower and broader than the signal of the 7-CH_3 group because of the high degree of coupling of 5-CH_3 with the proton in the 6 position (when R'' = H) in conformity with the higher degree of double bond character between the 5 and 6 positions as compared with the 6 and 7 positions. For the same reason, $J_{56} > J_{67}$ (5 and 7 Hz, respectively), and the introduction of a methyl group in the 6 position affects δ_{5}-H to a greater degree than δ_{7}-H; this has been previously noted [3]. All of these factors made it possible to make a choice of structures for the products of condensation of I with unsymmetrical carbonyl components; phenyl β-chlorovinyl ketone and 2-formylcyclohexanone give one isomer (IIk,l and IIu,v, respectively), whereas 1,1-dimethoxy-3-butanone and 3-chloro-2-methylbuten-2-al give mixtures of isomers in the following ratios (for the crude products): $II_m/II_n = 2/3$, $II_o/II_p = 2/1$, $II_q/II_r = 1/1$, and $II_s/II_t = 1/1$.

Strong acids (mineral acids or trifluoroacetic acid with heating) lead to cleavage of the oxadiazole ring of salts II at the $O-C_{(2)}$ bond to give 1-acylamino-2-pyrimidinones (III), which can subsequently be hydrolyzed to 1-amino-2-pyrimidinone (IV). The reaction occurs most readily when R = H. Inasmuch as salts II are obtained from 5-amino-1,3,4-oxadiazoles I and β-diketones in the presence of perchloric acid, one can, depending on the conditions, obtain either II or III or II and III successively by this reaction.

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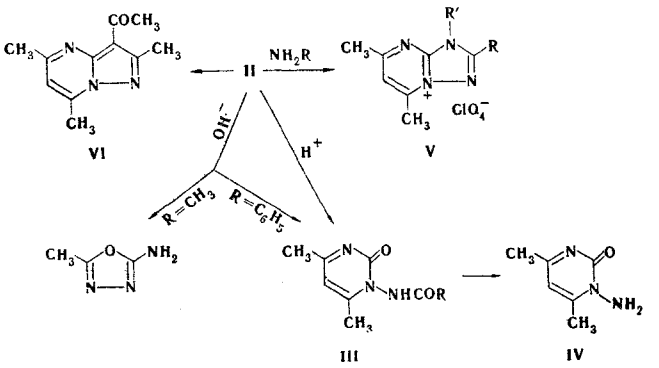

Refluxing a solution of 5-amino-2-methyl-1,3,4-oxadiazole (Ib) and acetylacetone in trifluoroacetic acid gave a trifluoroacetate, the perchlorate of which is identical to the perchlorate of IIIb. Salts of III were also obtained by acylation of IIu,v with formic acid (in the presence of benzoyl chloride) ($R = CH_3$), and benzoyl chloride ($R = C_6H_5$).

The signals of the pyrimidine methyl groups in the PMR spectra of the salts of III coincide (when $R = C_6H_5$), almost coincide ($R = H$), or have chemical shifts of slightly different magnitude ($R = CH_3$) and are observed at 2.4 ppm, whereas in the PMR spectrum of amino derivative IV they again diverge and are found at 2.28 and 2.47 ppm; in the latter case, the 4-CH_3 signal is found at weaker field, inasmuch as acylation of the amino group in IV may have a stronger effect on the 6-methyl group than on the 4-methyl group.

Deamination under the influence of nitrous acid to 4,6-dimethyl-2-pyrimidinone, identical to a genuine sample, also confirms the structure of the salt of IV. Base IIIc was obtained from its salt by treatment with ammonia.

On reaction with II, alkaline agents cleave either the pyrimidine ring (when $R = CH_3$) or the oxadiazole ring (when $R = C_6H_5$); this is probably associated with the difference in the electronic natures of the substituents. In the first case, one obtains 5-amino-2-methyl-1,3,4-oxadiazole, whereas in the second case, just as in the reaction of ammonium hydroxide with the salt of IIIc, base IIIc is obtained.

Like monocyclic quaternary oxadiazolium salts and 1,3,4-oxadiazolo[3,2-*a*]pyridinium derivatives [4], salts II react in acetic acid with aniline, hydrazine, and phenylhydrazine to give sym-triazolo[1,5-*a*]-pyrimidinium derivatives V. The structure of V is confirmed by their PMR spectra; salt Ve was also obtained by alternative synthesis by condensation of 4,5-diamino-3-benzyl-sym-triazolium perchlorate with acetylacetone by the method in [5]. Salt Vc was converted to the previously described [6] 2,5,7-trimethyl-sym-triazolo[1,5-*a*]pyrimidine by the action of nitrous acid, and this proves its structure.

The same compound – 3-acetyl-2,5,7-trimethylpyrazolo[1,5-*a*]pyrimidine (VI) – was obtained by the action of acetylacetone and potassium tert-butoxide on salts IIb and IIc by the method in [4].

EXPERIMENTAL

The PMR spectra of trifluoroacetic acid solutions of the compounds were recorded with a ZKR-60 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer.

2-Amino-1,3,4-oxadiazole. This compound was obtained from 1-formylthiosemicarbazide and PbO [7]. The remaining amines were obtained from the hydrazides of the corresponding acids and BrCN [8-10]. Perchlorates I were obtained by treatment of the bases with 57 or 42% perchloric acid (in the latter case it was necessary to evaporate the solution in air at room temperature) and were recrystallized from acetic acid. Salt Ia had mp 169°. Found: Cl 18.9%. $C_2H_3N_3O \cdot HClO_4$. Calculated: Cl 19.1%. PMR spectrum (in DMSO): 8.88 (5-H) and 10.18 (NH_2) ppm. Salt Ib had mp 95°. Found: Cl 17.7%. $C_3H_5N_3O \cdot HClO_4$. Calculated Cl 17.7%. Salt Ic had mp 189°, and If had mp 216°.

Compounds IIg and III were recrystallized from dilute ethanol, IIIb, c, e, f and VI were recrystallized from ethanol, and III and IIIa were recrystallized from acetone, and the remaining products, which are presented in Table 1, were recrystallized from acetic acid.

TABLE 1. Characteristics of the Products Obtained

Compound	R	R′	R″	R‴	mp, °C	Empirical formula	Cl, % found	Cl, % calc.	Yield, %
IIa	H	CH_3	H	CH_3	151	$C_7H_8ClN_3O_5$	14,1	14,2	90
b	CH_3	CH_3	H	CH_3	186	$C_8H_{10}ClN_3O_5$	13,3	13,4	76[a], 31[b]
c	C_6H_5	CH_3	H	CH_3	237	$C_{13}H_{12}ClN_3O_5$	10,9	10,9	80
d	$CH_2C_6H_5$	CH_3	H	CH_3	160	$C_{14}H_{14}ClN_3O_5$	10,4	10,4	51[a], 28[b]
e	$CO_2C_6H_5$	CH_3	H	CH_3	167	$C_{10}H_{12}ClN_3O_7$	11,2	11,0	26
f	o-C_6H_4—OH	CH_3	H	CH_3	246	$C_{13}H_{12}ClN_3O_6$	10,6	10,4	87
g	C_6H_5	CH_3	CH_3	CH_3	275	$C_{14}H_{14}ClN_3O_5$	10,2	10,4	92
h	CH_3	H	H	H	204	$C_6H_6ClN_3O_5$	15,0	15,0	36
i	C_6H_5	H	H	H	283	$C_{11}H_8ClN_3O_5$	11,9	11,9	40
j	CH_3	H	Br	H	241	$C_6H_5BrClN_3O_5$	13,5[c]	13,4	48
k	CH_3	CH_3	H	C_6H_5	186	$C_{12}H_{10}ClN_3O_5$	11,3	11,0	52
l	C_6H_5	H	H	C_6H_5	257	$C_{17}H_{12}ClN_3O_5$	9,4	9,5	34
u	CH_3	$(-CH_2-)_4$		H	202	$C_{10}H_{12}ClN_3O_5$	12,8	12,9	89
v	C_6H_5	$(-CH_2-)_4$		H	235	$C_{15}H_{14}ClN_3O_5$	10,4	10,6	95
IIIa	H	—	—	—	185	$C_7H_9N_3O_2 \cdot HClO_4$	13,4	13,2	47[a] 98[b]
b	CH_3	—	—	—	205	$C_8H_{11}N_3O_2 \cdot HClO_4$	12,7	12,6	43[a], 98[b]
c	C_6H_5	—	—	—	215	$C_{13}H_{13}N_3O_2 \cdot HClO_4$	12,1[c]	12,2	50
IV	—	—	—	—	192	$C_6H_9N_3O \cdot HClO_4$	17,5[c]	17,5	50[a], 82[b]
Va	CH_3	C_6H_5	—	—	233	$C_{14}H_{15}ClN_4O_4$	11,0	10,9	93
b	C_6H_5	C_6H_5	—	—	257	$C_{19}H_{17}ClN_4O_4$	8,8	8,8	90
c	CH_3	NH_2	—	—	182	$C_8H_{12}ClN_5O_4$	12,6	12,4	48
d	C_6H_5	NH_2	—	—	217	$C_{13}H_{14}ClN_5O_4$	10,3	10,4	33
e	$CH_2C_6H_5$	NH_2	—	—	172	$C_{14}H_{17}ClN_5O_4$	10,2	10,0	42
f	C_6H_5	NHC_6H_5	—	—	184	$C_{19}H_{18}ClN_5O_4$	8,5	8,5	88
VI	—	—	—	—	226	$C_{11}H_{13}N_3O$	20,5[c]	20,7	61[a], 43[b]

[a]By method A.
[b]By method B.
[c]N, %.

TABLE 2. PMR Spectra (δ)

Compound	R	R′	R″	R‴	Compound	R	R′	R″	R‴
IIa	8,92	2,65	7,58	2,73	IIu	2,54	2,6—3,2		5,88
b	2,60	2,60	7,42	2,67			1,6—1,9		
c	8,0	2,61	7,53	2,74	v	7,9	2,6—3,2		8,63
	7,5					7,4	1,5—1,8		
d	7,03	2,54	7,36	2,63	IIIa	—	2,44	6,63	2,41
	4,17				b	2,10	2,43	6,66	2,38
e	4,45	2,68	7,63	2,76	c	7,6	2,43	6,63	2,43
	1,17					7,3			
f	6,8—7,9	2,60	7,47	2,70	IV	—	2,47	5,42	2,28
g	—	2,57	2,25	2,73	Va[d]	2,31	2,46	7,1—7,5	2,70
h	2,64	8,9—9,2	7,88	8,9—9,2	b[d]	7,1—7,5	2,48	7,1—7,5	2,78
					c	2,53	2,56	7,22	2,63
i	8,0	9,13[a]	8,0	9,18[b]		or	or		
	7,5					2,56	2,53		
j	2,61	9,31	—	9,40	e	7,0	2,51	7,14	2,66
k	2,58	2,85[a]	7,86[a]	7,8		4,23			
				7,4	f		2,44		2,73
m		8,68	2,21	2,68	VIe	2,58	2,75	7,07	2,82
n		2,58	2,28	8,58					
o	—	8,73	2,25	2,80					
p	—	2,63	2,25	8,73					
q	2,62	8,80[a]	—	2,75					
r	2,57	2,67	—	8,72[c]					
s	—	—	—	2,81					
t	—	2,67	—	—					

[a]J = 5 Hz.
[b]J = 6.5 Hz.
[c]J = 7 Hz.
[d]The chemical shift of the protons of the V [sic] group at 7.1-7.5 ppm.
[e]The chemical shift of the CH_3CO protons is found at 2.5 ppm.

5,7-Dimethyl-1,3,4-oxadiazolo[3,2-*a*]pyrimidinium Perchlorate (IIa). A mixture of 0.37 g (0.002 mole) of salt Ia and 0.4 ml (0.004 mole) of acetylacetone was heated on a water bath for 10 min, after which it was cooled, and the crystallized mass was washed with acetic acid and ether.

2,5,7-Trimethyl-1,3,4-oxadiazolo[3,2-*a*]pyrimidinium Perchlorate (IIb). A) A mixture of 0.80 g (0.004 mole) of salt Ib, 1 ml (0.01 mole) of acetylacetone, and 2 ml of acetic acid was refluxed for 20 min, after which it was cooled, and the precipitated product was removed by filtration and washed with acetic acid and ether. Compound IIf was similarly obtained.

B) A mixture of 0.20 g (0.002 mole) of base Ib, 0.3 ml (0.003 mole) of acetylacetone, and 0.4 ml of 42% perchloric acid was refluxed for 20 min. It was then cooled, 2 ml of acetic acid and excess ether were added successively, and the resulting precipitate was removed by filtration. Compound IId was similarly obtained.

2-Phenyl-5,7-dimethyl-1,3,4-oxadiazolo[3,2-*a*]pyrimidinium Perchlorate (IIc). A mixture of 13 g (0.05 mole) of salt Ic and 6 ml (0.06 mole) of acetylacetone was heated to 110°, during which an exothermic reaction ensued. The mixture was then cooled, and the crystalline mass was washed with acetic acid and ether.

2-Benzyl-5,7-dimethyl-1,3,4-oxadiazolo[3,2-*a*]pyrimidinium Perchlorate (IId). A) A mixture of 1.38 g (0.008 mole) of base Id, 1 ml (0.01 mole) of acetylacetone, and 8 ml of a solution obtained from 34 ml of 42% perchloric acid and 150 ml of acetic anhydride was refluxed for 30 min. The following day, the precipitated product was removed by filtration and washed with acetic acid and ether.

Compound IIe was similarly obtained.

2-Phenyl-5,6,7-trimethyl-1,3,4-oxadiazolo[3,2-*a*]pyrimidinium Perchlorate (IIg). A mixture of 4.0 g (0.25 mole) of Ig and 3 ml (0.026 mole) of 3-methylacetylacetone was heated at 150-160° for 1 h, after which it was cooled, and the resulting precipitate was removed by filtration and washed with acetic acid and ether.

2-Methyl- and 2-Phenyl-1,3,4-oxadiazolo[3,2-*a*]pyrimidinium Perchlorates (IIh, i). These compounds were obtained by refluxing 0.003 mole of salt Ib or Ic with 0.005 mole of 1,1,3,3'-tetraethoxypropane in 1 ml of acetic acid.

6-Bromo-2-methyl-1,3,4-oxadiazolo[3,2-*a*]pyrimidinium Perchlorate (IIj). A mixture of 0.4 g (0.002 mole) of salt Ib and 0.9 ml (0.003 mole) of 2-bromo-1,1,3,3-tetraethoxypropane was heated on a water bath. After 2-3 min, the product precipitated from the hot solution.

5-Phenyl-2-methyl- and 2,5-Diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyrimidinium Perchlorate (IIk, l). A mixture of 0.002 mole of the salt (Ib or Ic) and phenyl β-chlorovinyl ketone in 2 ml of acetic acid was heated for a few minutes on a water bath and allowed to stand overnight at room temperature. The product was precipitated by the addition of ether and washed with acetic acid and ether.

2-Methyl- and 2-Phenyl-6,7,8,9-tetrahydro-1,3,5-oxadiazolo[3,2-*a*]quinazolinium Perchlorate (IIu, v). A mixture of 0.003 mole of salt Ib or Ic and 0.004 mole of 2-formylcyclohexanone was heated to the boiling point, after which it was allowed to stand overnight. The following day the product was removed by filtration.

Mixtures of salts IIm and IIn, IIo and IIp, IIq and IIr, and IIs and IIt were similarly obtained from 3-chloro-2-methylbuten-2-al and 1,1-dimethoxybutan-3-one, except that ethanol was used in place of acetic acid for the preparation of IIm-p, and the mixture was not allowed to stand overnight in the preparation of II q-t but was refluxed for 10 min.

Action of Alkali on Salts II. A) A 0.52-g (0.002 mole) sample of salt IIb was added to a solution of 0.20 g (0.005 mole) of sodium hydroxide in 1 ml of water, and the mixture was warmed to dissolve the salt, after which it was evaporated to dryness at room temperature. The residue was extracted with boiling ethyl acetate, and the solvent was removed from the extract to give 0.32 g (80%) of 5-amino-2-methyl-1,3,4-oxadiazole.

B) Concentrated ammonium hydroxide (10 ml) was added with stirring to a solution of 0.99 g (0.003 mole) of salt IIc in 20 ml of water, during which an orange oil, which soon solidified, was liberated (0.23 g). The filtrate was evaporated to dryness at room temperature, and the residue was extracted with hot isopropyl alcohol. Evaporation of the extract gave another 0.32 g of base IIIc. The overall yield of product with mp 214° (from isopropyl alcohol) was 0.55 g (76%). Found: N 17.0%. $C_{13}H_{13}N_3O_2$. Calculated: N 17.3%.

Preparation of Styryls. A) A mixture of 0.33 g (0.001 mole) of salt IIc, 0.15 g (0.001 mole) of p-dimethylaminobenzaldehyde, and 2 ml of acetic anhydride was refluxed for 10 min, after which the precipitated dye was removed by filtration and washed with acetic acid and ether. The yield of 5-(p-dimethylaminostyryl)-2-phenyl-7-methyl-1,3,4-oxadiazolo-[3,2-*a*]pyrimidinium perchlorate, with mp 241° (from acetic acid), was 0.42 g (91%). PMR spectrum: 3.18 (6H) and 2.66 ppm (7-CH_3). Found: Cl 8.0%. $C_{22}H_{21}ClN_4O_5$. Calculated: Cl 7.8%.

B) A mixture of 0.33 g (0.001 mole) of salt IIc, 0.45 g (0.003 mole) of p-dimethylaminobenzaldehyde, and 4 ml of acetic anhydride was refluxed for 15 min, after which the precipitated dye was removed by filtration and washed with acetic acid and ether to give 0.52 g (88%) of a distyryl with mp 320° (from nitrobenzene). PMR spectrum: 3.20 ppm (6H). Found: Cl 6.2%. $C_{31}H_{30}ClN_5O_5$. Calculated: Cl 6.0%.

1-Formylamino-4,6-dimethyl-2-pyrimidinone (IIIa) Hydroperchlorate. A) A mixture of 0.93 g (0.006 mole) of Ia, 0.6 ml (0.006 mole) of acetylacetone, and 2 ml of acetic acid was refluxed for 15 min, after which the product was precipitated by the addition of ether.

B) A mixture of 0.48 g (0.002 mole) of amine IV, 1 ml of 85% formic acid, and 0.7 ml of benzoyl chloride was heated to the boiling point. The mixture was then cooled and the product was precipitated by the addition of ether.

1-Acetamido-4,6-dimethyl-2-pyrimidinone (IIIb) Hydroperchlorate. A) A mixture of 2.50 g (0.025 mole) of oxadiazole Ib, 4.5 ml (0.025 mole) of 42% perchloric acid, and 3 ml (0.03 mole) of acetylacetone was refluxed for 1 h. The mixture was then cooled, and the product was precipitated by the addition of ether.

B) A 0.48-g sample of amine IV was dissolved in 1 ml of acetic anhydride; the mixtures became warm and rapidly solidified to a crystalline mass. The mixture was cooled, and the product was washed with ether. The same product was also obtained by heating a mixture of amine IV, acetyl chloride, and acetic acid on a water bath for several minutes and also by refluxing equimolecular amounts of 5-amino-2-methyl-1,3,4-oxadiazoles and acetylacetone in trifluoroacetic acid with subsequent conversion of the trifluoroacetate (recrystallized from acetone) to the perchlorate by means of perchloric acid.

1-Benzamido-4,6-dimethyl-2-pyrimidinone (IIIc) Hydroperchlorate. A) A mixture of 4.95 g (0.03 mole) of oxadiazole Ic, 3.0 ml (0.03 mole) of acetylacetone, and 5.4 ml of 42% perchloric acid was refluxed for 2 h, after which the solution was evaporated on a water bath, and the residue was washed with ether.

B) A mixture of 0.48 g (0.002 mole) of amine IV, 0.7 ml of benzoyl chloride, and 2 ml of trifluoroacetic acid was heated to the boiling point, after which it was cooled, and the product was precipitated by the addition of ether. Concentrated ammonium hydroxide (10 ml) was added to a solution of 0.72 g of salt IIIc in 10 ml of water, and the resulting solution was evaporated to dryness at room temperature. The residue was extracted with boiling isopropyl alcohol, and the solvent was removed from the extract by distillation to give 0.43 g (60%) of base IIIc, which was identical to the base obtained above.

1-Amino-4,6-dimethyl-2-pyrimidinone (IV) Hydroperchlorate. A) A mixture of 4.95 g (0.05 mole) of oxadiazole Ib, 6 ml (0.06 mole) of acetylacetone, and 9 ml of 42% perchloric acid was refluxed for 1 h, after which it was cooled, and 6 ml of acetic acid and excess ether were added successively. The resulting precipitate was removed by filtration and washed with acetic acid and ether.

B) A mixture of 0.30 g (0.009 mole) of IIIc and 2 ml of 42% perchloric acid was refluxed for 3 h, after which 2 ml of acetic acid and excess ether were added.

The same product was obtained by heating salts IIa-c with 42% perchloric acid.

4,6-Dimethyl-2-pyrimidinone. A solution of 0.62 g (0.009 mole) of sodium nitrite in 2 ml of water was added dropwise at 0° to a solution of 2.1 g (0.009 mole) of the hydroperchlorate of IV in 10 ml of trifluoroacetic acid, after which the mixture was filtered, and the product was precipitated from the filtrate by the addition of ether. The precipitate was removed by filtration and washed with acetic acid and ether to give 0.98 g (50%) of 4,6-dimethyl-2-pyrimidinone hydroperchlorate with mp 254° (from acetic acid). The product was identical to the salt obtained from a genuine sample of 4,6-dimethyl-2-pyrimidinone and perchloric acid.

Reactions of Salts II with Aniline, Hydrazine, and Phenylhydrazine. A mixture of 0.002 mole of salt II and 0.003-0.004 mole of the nucleophilic reagent was refluxed in 2-4 ml of acetic acid for 15 min, after

which the mixture was cooled, and the resulting precipitate was removed by filtration and washed with acetic acid and ether.

3-Acetyl-2,5,7-trimethylpyrazolo[1,5-*a*]pyrimidine (VI). A 0.005-mole sample of salt IIb or IIc and a solution of 0.01 mole of potassium in 8 ml of tert-butyl alcohol were added successively to a solution of 0.0075 mole of acetylacetone in 5 ml of tert-butyl alcohol, after which the mixture was refluxed for 45 min, and the hot solution was filtered. The filtrate was cooled to precipitate VI, which was removed by filtration and washed with ether.

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ACTION OF ALKALI METALS IN LIQUID AMMONIA ON SUBSTITUTED THIOPHENES

III.* PREPARATION OF AMINO KETONES OF THE ALIPHATIC SERIES FROM 2-(ω-DIALKYLAMINOALKYL)THIOPHENES

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The action of lithium and alcohols in liquid ammonia on α-substituted thiophenes with subsequent hydrolysis of the products leads to conversion of the thiophene fragment of the molecule to a butyryl group. A number of amino ketones of the aliphatic series were obtained from α-(ω-dialkylaminoalkyl)thiophenes.

Currently one of the most nearly universal methods for the preparation of derivatives of the aliphatic and cycloparaffin series, especially those with long straight and branched chains of carbon atoms, is reductive desulfuration of substituted thiophenes with Raney nickel. This method, as a rule, proves to be effective in all cases and leads to the conversion of the thiophene ring to a hydrocarbon chain made up of four carbon atoms. Another reductive agent – sodium or lithium in liquid ammonia [1, 2] – acts on α-alkyl-, α-(ω-hydroxyalkyl)-, and α-(ω-carboxyalkyl)-substituted thiophenes in such a way that, in addition to hydrogenation of the unsaturated bonds, the ring is cleaved at the bond between the sulfur atom and the unsubstituted ring carbon atom. Thus in all of the cases that we investigated we observed (after hydrolysis of the reaction mixture) the formation of compounds having a butyryl group.

*See [1] for communication II.

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