

## Pyridazinones. I.

### Preparation of 2,4-disubstituted 5-hydroxy-3(2*H*)-pyridazinones and 2,5-disubstituted 4-hydroxy-3(2*H*)-pyridazinones

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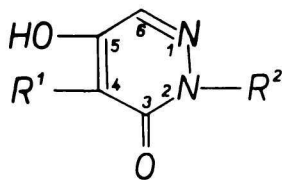
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The synthesis of 2,4-disubstituted 5-hydroxy-3(2*H*)-pyridazinones and 2,5-disubstituted 4-hydroxy-3(2*H*)-pyridazinones by alkali hydrolysis of 2-substituted 4,5-dihalo-3(2*H*)-pyridazinones, 2-substituted 4,5-dialkoxy-3(2*H*)-pyridazinones, 2-substituted 4-alkoxy-5-halo-3(2*H*)-pyridazinones, 2-substituted 4-halo-5-alkoxy-3(2*H*)-pyridazinones, 2-substituted 4-halo(alkylthio)-5-alkylthio(halo)-3(2*H*)-pyridazinones or by the reaction of sodium iodide with 2-substituted 4,5-dialkoxy(dialkylthio)-3(2*H*)-pyridazinones is described.

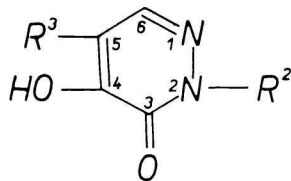
Описывается синтез 2,4-дизамещенных 5-гидрокси-3(2*H*)-пиридазинов и 2,5-дизамещенных 4-гидрокси-3(2*H*)-пиридазинов при помощи щелочного гидролиза 2-замещенных 4,5-дигалоген-3(2*H*)-пиридазинов, 2-замещенных 4,5-диалкокси-3(2*H*)-пиридазинов, 2-замещенных 4-алкокси-5-галоген-3(2*H*)-пиридазинов, 2-замещенных 4-галоген-5-алкокси-3(2*H*)-пиридазинов и 2-замещенных 4-галоген(алкилтио)-5-алкилтио(галоген)-3(2*H*)-пиридазинов или же при помощи реакции иодистого натрия с 2-замещенными 4,5-диалкокси(диалкилтио)-3(2*H*)-пиридазинами.

It is known that by the reaction of 2-phenyl-4,5-dichloro-3(2*H*)-pyridazinone with sodium methoxide in methanol and with sodium ethoxide in ethanol under reflux, beside other substances also 2-phenyl-4-methoxy-5-hydroxy-3(2*H*)-pyridazinones and 2-phenyl-4-ethoxy-5-hydroxy-3(2*H*)-pyridazinones, respectively, are obtained [1]. Similarly, the reaction of 2-phenyl-4-chloro-5-methylthio-3(2*H*)-pyridazinone with 10% sodium hydroxide in water at 130°C under pressure results in the formation of 2-phenyl-4-hydroxy-5-methylthio-3(2*H*)-pyridazinone, 2-phenyl-4-hydroxy-5-methylthio-3(2*H*)-pyridazinone, and 2-phenyl-4-methylthio-5-hydroxy-3(2*H*)-pyridazinone [2]. Alkali hydrolysis of 2-phenyl-4,5,6-trichloro-3(2*H*)-pyridazinone affords 2-phenyl-4,6-dichloro-5-hydroxy-3(2*H*)-pyridazinone, and 2-phenyl-4,6-dichloro-3(2*H*)-pyridazinone gives 2-phenyl-4-hydroxy-6-chloro-3(2*H*)-pyridazinone [3].

The preparation of 2,4-disubstituted 5-hydroxy-3(2*H*)-pyridazinones (*A*) and 2,5-disubstituted 4-hydroxy-3(2*H*)-pyridazinones (*B*) is described in this work.



A



B

The compounds of the structure *A* were prepared by the hydrolysis of 2-substituted 4,5-dialkoxy-3(2*H*)-pyridazinone, 4-alkylthio-5-halo-3(2*H*)-pyridazinone, 4,5-dihalo-3(2*H*)-pyridazinone, and 4-halo-5-alkoxy-3(2*H*)-pyridazinone with alkali hydroxide. The compounds of the structure *B* were prepared by the hydrolysis of 2-substituted 4-halo-5-alkylthio-3(2*H*)-pyridazinones, 4-alkoxy-5-halo-3(2*H*)-pyridazinone with alkali hydroxide and by the reaction of 2-substituted 4,5-dialkoxy-3(2*H*)-pyridazinones with potassium iodide.

It is interesting that in 2-substituted 4-alkoxy-5-chloro-3(2*H*)-pyridazinone and 4-chloro-5-alkoxy-3(2*H*)-pyridazinone only the alkoxy group was hydrolyzed while in the hydrolysis of 2-substituted 4-alkylthio-5-chloro-3(2*H*)-pyridazinone chlorine was substituted similarly as in the case of 2-substituted 4-chloro-5-alkylthio-3(2*H*)-pyridazinone. The hydrolysis of alkylthio derivatives proceeded much slower than that of the alkoxy derivatives. The time of hydrolysis could be reduced by using water—ethylene glycol as the reaction medium in the ratio of 1:1 or 1:2. The hydrolysis of the alkoxy derivatives proceeded for 6—8 hrs while the hydrolysis of the alkylthio derivatives required 16—24 hrs at the same conditions.

2-Substituted 4,5-dihalo-3(2*H*)-pyridazinone afforded only 5-hydroxy derivative on hydrolysis which proceeded for 4—8 hrs. In this case it was necessary to use at least a two-fold excess of the alkali hydroxide.

Another interesting finding was that alkali hydrolysis of 2-phenyl-4,5-dialkylthio-3(2*H*)-pyridazinones yielded 2-phenyl-4-alkylthio-5-hydroxy-3(2*H*)-pyridazinone while on hydrolysis of 2-methyl-4,5-dialkylthio-3(2*H*)-pyridazinones, 2-methyl-4-hydroxy-5-alkylthio-3(2*H*)-pyridazinone was formed.

Treatment of 2-substituted 4,5-dialkoxy-3(2*H*)-pyridazinone with sodium iodide in dimethylformamide, propanone or butanone resulted in the formation of 2-substituted 4-hydroxy-5-alkoxy-3(2*H*)pyridazinone. The reaction rate de-

pended on the length of the alkoxy group in the position 5. With the increasing length of the alkoxy group, the yield and the reaction rate decreased. It is remarkable that the substituent  $R^2$  did not affect the course of the reaction.

The structure of the prepared compounds (*A* and *B*) was confirmed by i.r., u.v., n.m.r. as well as Raman and mass spectra. The study of the structures of the above compounds will be the subject of our next communication.

### Experimental

Physical constants and data of elemental analysis of the synthesized compounds are presented in Tables 1 and 2.

#### *4-Chloro-5-hydroxy-3(2H)-pyridazinone I*

To 20% sodium hydroxide (800 ml) 4,5-dichloro-3(2H)-pyridazinone (1 mole) was added and the mixture was stirred for 18 hrs at boiling. The insoluble part was filtered off and the filtrate was acidified with hydrochloric acid. After 4 days staying the precipitated substance was filtered and purified by crystallization.

#### *Compounds II—XIX*

To alkali hydroxide (0.25 mole) in water (100 ml) 2-substituted 4,5-dihalo-3(2H)-pyridazinone (0.1 mole) was added under stirring. The reaction mixture was slowly heated to reflux and stirred for 6—16 hrs. The insoluble part was filtered off and the filtrate was acidified with hydrochloric acid under stirring. The precipitated solid was filtered and purified by crystallization.

#### *Compounds XXIX, XXXI, XXXIII—XXXVIII*

To alkali hydroxide (0.2—0.3 mole) dissolved in water (120 ml) or in a mixture of water (40 ml) and ethylene glycol (80 ml) 2-phenyl-4,5-dialkoxy-3(2H)-pyridazinone (0.1 mole) was added and the reaction mixture was stirred for 6—80 hrs at boiling. Hydrochloric acid was added under stirring so as to attain pH 1. The precipitated substance was separated and crystallized.

#### *Compounds XXI, XXIII, XXV, XXVIII, and XXX*

To alkali hydroxide (0.3 mole) in a mixture of water (80 ml) and ethylene glycol (160 ml) 2-substituted 4-alkylthio-5-chloro-3(2H)-pyridazinone (0.1 mole) was added and the reaction mixture was stirred for 8 hrs at boiling. After pouring it into water (600 ml) hydrochloric acid was added so as to attain pH 1. The precipitate was filtered and purified by crystallization.

#### *Compounds XX, XXII, XXVII, XLI, XLIII, and XLVII*

To alkali hydroxide (1 mole) in water (300 ml) 2-alkyl-4,5-alkoxy-3(2H)-pyridazinone (0.4 mole) was added and the reaction mixture was stirred for 6—30 hrs at boiling. The reaction mixture was

Table 1

## Characterization of the compounds A

No.	R <sup>1</sup>	R <sup>2</sup>	Formula	M	Calculated/found		Yield %	M.p., °C Solvent
					% Cl	% N		
I	Cl	H	C <sub>4</sub> H <sub>3</sub> ClN <sub>2</sub> O <sub>2</sub>	146.52	24.19 23.95	19.11 19.23	48.5	270—273 DMF
II	Cl	CH <sub>3</sub>	C <sub>5</sub> H <sub>5</sub> ClN <sub>2</sub> O <sub>2</sub>	160.55	22.15 22.08	17.44 17.16	84.3	254—258 EtOH
III	Br	CH <sub>3</sub>	C <sub>5</sub> H <sub>5</sub> BrN <sub>2</sub> O <sub>2</sub>	205.01	38.97 <sup>a</sup> 38.69	13.66 13.70	64.8	283—284 EtOH
IV	Cl	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>7</sub> ClN <sub>2</sub> O <sub>2</sub>	174.56	20.33 20.08	16.04 15.82	73.4	224—228 EtOH
V	Cl	C <sub>3</sub> H <sub>7</sub>	C <sub>7</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>2</sub>	188.60	18.80 19.04	14.85 14.53	63.3	187—191 EtOH
VI	Cl	CH(CH <sub>3</sub> ) <sub>2</sub>	C <sub>7</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>2</sub>	188.60	18.80 19.02	14.85 14.62	46.3	240—244 EtOH
VII	Cl	CH <sub>2</sub> —CH=CH <sub>2</sub>	C <sub>7</sub> H <sub>7</sub> ClN <sub>2</sub> O <sub>2</sub>	186.59	19.00 19.39	14.96 14.71	41.0	166—169 EtOH
VIII	Cl	C <sub>4</sub> H <sub>9</sub>	C <sub>8</sub> H <sub>11</sub> ClN <sub>2</sub> O <sub>2</sub>	202.62	17.50 17.38	13.80 14.02	67.6	153—155 EtOH
IX	Cl	CH <sub>2</sub> —CH=C—CH <sub>3</sub>   Cl	C <sub>8</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	235.06	30.18 29.91	11.92 12.03	62.2	149—151 EtOH
X	Cl	C <sub>8</sub> H <sub>17</sub>	C <sub>12</sub> H <sub>19</sub> ClN <sub>2</sub> O <sub>2</sub>	258.53	13.68 13.90	10.83 10.80	41.1	117—120 EtOH

Table I (Continued)

No.	R <sup>1</sup>	R <sup>2</sup>	Formula	M	Calculated/found		Yield %	M.p., °C Solvent
					% Cl	% N		
XI	Cl	CH <sub>2</sub> -O-CH <sub>3</sub>	C <sub>6</sub> H <sub>7</sub> ClN <sub>2</sub> O <sub>3</sub>	190.58	18.61 19.07	14.70 14.50	61.58	180-183 EtOH
XII	Cl	CH <sub>2</sub> -S-C <sub>2</sub> H <sub>5</sub>	C <sub>7</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>2</sub> S	220.61	16.12 16.43	12.75 13.04	36.8	230-232 Dioxan
XIII	Cl	C <sub>6</sub> H <sub>11</sub>	C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub> O <sub>2</sub>	228.66	15.50 15.97	12.25 12.46	91.2	257-259 Dioxan
XIV	Cl	C <sub>6</sub> H <sub>5</sub>	C <sub>10</sub> H <sub>7</sub> ClN <sub>2</sub> O <sub>2</sub>	222.62	15.91 15.96	12.57 12.41	89.7	266-269 EtOH
XV	Cl	C <sub>6</sub> H <sub>4</sub> -4-CH <sub>3</sub>	C <sub>11</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>2</sub>	236.64	14.98 15.07	11.83 12.10	72.0	296-298 EtOH
XVI	Cl	C <sub>6</sub> H <sub>4</sub> -4-Cl	C <sub>10</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	257.08	27.58 27.35	10.89 10.80	68.9	275-278 EtOH
XVII	Cl	C <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub>	C <sub>10</sub> H <sub>6</sub> ClN <sub>2</sub> O <sub>4</sub>	267.63	13.24 12.95	15.70 15.45	20.5	265-269 DMF
XVIII	Cl	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>2</sub>	236.64	14.98 14.91	11.83 11.62	63.2	215-218 EtOH
XIX	Br <sup>b</sup>	CH <sub>2</sub> OCONHC <sub>6</sub> H <sub>4</sub> -3-Cl	C <sub>12</sub> H <sub>9</sub> BrClN <sub>3</sub> O <sub>4</sub>	360.56	9.58 9.71	7.78 8.12	74.7	222-224 EtOH

Table 1 (Continued)

No.	R <sup>1</sup>	R <sup>2</sup>	Formula	M	Calculated/found			Yield %	M.p., °C Solvent
					% C	% H	% N		
XX	CH <sub>3</sub> O	CH <sub>3</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>	156.13	46.06	5.12	17.92	72.2	169—170 CHCl <sub>3</sub>
					46.20	5.18	17.84		
XXI <sup>a</sup>	CH <sub>3</sub> S	CH <sub>3</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> S	172.19	41.84	4.64	16.22	81.1	187—190 Dioxan
					41.61	4.52	16.01		
XXII	C <sub>2</sub> H <sub>5</sub> O	CH <sub>3</sub>	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>	170.16	49.48	5.91	16.47	75.5	140—142 Toluene
					49.02	5.70	16.29		
XXIII <sup>d</sup>	C <sub>2</sub> H <sub>5</sub> S	CH <sub>3</sub>	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S	186.22	45.14	5.37	15.03	69.4	122—125 Toluene
					44.85	5.21	15.18		
XXIV	C <sub>3</sub> H <sub>7</sub> O	CH <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	184.18	52.18	6.51	15.22	42.5	119—120 Benzene
					52.16	6.67	15.55		
XXV <sup>e</sup>	C <sub>3</sub> H <sub>7</sub> S	CH <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	200.24	47.98	6.03	13.99	81.2	107—109 Cyclohexane
					47.81	5.81	14.12		
XXVI	i-C <sub>3</sub> H <sub>7</sub> O	CH <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	184.18	52.18	6.51	15.22	31.2	138—140 Benzene
					51.94	6.23	15.18		
XXVII	CH <sub>3</sub> O	C <sub>6</sub> H <sub>11</sub>	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	224.36	58.75	7.11	12.50	56.2	163—165 Benzene
					58.63	6.82	12.32		
XXVIII <sup>f</sup>	C <sub>2</sub> H <sub>5</sub> S	C <sub>6</sub> H <sub>11</sub>	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S	254.42	56.64	7.07	11.01	74.1	123—125 Toluene
					56.29	6.88	10.88		
XXIX <sup>g</sup>	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>	218.20	60.34	4.57	12.82	79.2	182—184 Toluene
					60.61	4.82	12.80		

Table 1 (Continued)

No.	R <sup>1</sup>	R <sup>2</sup>	Formula	M	Calculated/found			Yield %	M.p., °C Solvent
					% C	% H	% N		
XXX <sup>a,m</sup>	CH <sub>3</sub> S	C <sub>6</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S	234.26	56.37 56.06	4.30 4.15	11.95 12.16	79.9	183—186 EtOH
XXXI <sup>f</sup>	C <sub>2</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	232.22	61.95 62.12	5.13 4.88	12.04 11.58	88.3	147—149 Toluene
XXXII <sup>h</sup>	C <sub>2</sub> H <sub>5</sub> S	C <sub>6</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	248.38	58.02 57.81	4.87 4.55	11.28 11.05	89.7	140—142 EtOH
XXXIII	$\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{N}-\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$	C <sub>6</sub> H <sub>5</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>	259.23	60.31 59.82	5.02 4.89	16.19 15.88	39.0	193—195 Benzene
XXXIV <sup>f</sup>	C <sub>2</sub> H <sub>5</sub> SCH <sub>2</sub> CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub>	C <sub>14</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub> S	291.33	58.01 57.78	5.15 5.21	9.62 9.65	40.0	53—56 Benzene
XXXV	OC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	280.26	68.51 68.81	4.27 4.50	9.98 10.18	62.0	217—220 EtOH
XXXVI	OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	294.28	69.45 69.72	4.76 4.91	8.62 8.80	43.5	150—154 MeOH
XXXVII	OC <sub>2</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	324.30	66.56 66.19	4.92 4.81	8.96 8.59	49.2	72—74 MeOH
XXXVIII	CH <sub>3</sub> O	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	232.22	62.01 61.88	5.17 5.02	12.05 12.27	65.0	147—149 Toluene

a) % Br; b) % Br 22.82/23.11; c) % S 18.61/18.36; d) % S 17.17/16.90; e) % S 16.01/15.78; f) % S 12.57/12.45; g) % S 13.63/13.44; h) % S 12.86/12.63; i) % S 10.92/10.45; j) Ref. [1] 273—274°C; k) [1] 182—184°C; l) [1] 167—168°C; m) [2] 188°C.

Table 2

## Characterization of the compounds B

No.	R <sup>3</sup>	R <sup>2</sup>	Formula	M	Calculated/found			Yield %	M.p., °C Solvent
					% C	% H	% N		
XXXIX	Cl	CH <sub>3</sub>	C <sub>3</sub> H <sub>5</sub> ClN <sub>2</sub> O <sub>2</sub>	160.55	—	—	17.44 17.14	91.5	213—216 Toluene
XL	Br	CH <sub>3</sub>	C <sub>3</sub> H <sub>5</sub> BrN <sub>2</sub> O <sub>2</sub>	205.01	—	—	13.66 13.43	76.5	180—184 Toluene
XLI	CH <sub>3</sub> O	CH <sub>3</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>	156.13	46.06 46.31	5.12 5.02	17.92 17.61	19.5	162—163 Toluene
XLII <sup>a</sup>	CH <sub>3</sub> S	CH <sub>3</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> S	172.19	41.84 41.54	4.64 4.32	16.22 16.01	77.9	155—158 Toluene
XLIII	C <sub>2</sub> H <sub>5</sub> O	CH <sub>3</sub>	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>	170.16	49.48 49.16	5.91 5.82	16.47 16.22	33.9	132—135 Toluene
XLIV <sup>b</sup>	C <sub>2</sub> H <sub>5</sub> S	CH <sub>3</sub>	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S	186.22	45.14 45.34	5.37 5.60	15.03 14.87	61.6	153—155 MeOH
XLV	C <sub>3</sub> H <sub>7</sub> O	CH <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	184.18	52.18 52.14	6.51 6.66	15.22 15.48	19.2	124—127 EtOH
XLVI <sup>c</sup>	C <sub>3</sub> H <sub>7</sub> S	CH <sub>3</sub>	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	200.24	47.98 48.11	6.03 5.94	13.99 14.22	81.2	118—121 Cyclohexane
XLVII	CH <sub>3</sub> O	C <sub>6</sub> H <sub>11</sub>	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	224.26	58.75 58.54	7.11 7.01	12.50 12.32	66.9	121—123 Cyclohexane
XLVIII <sup>d</sup>	C <sub>2</sub> H <sub>5</sub> S	C <sub>6</sub> H <sub>11</sub>	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S	254.42	56.64 56.33	7.07 6.85	11.01 11.32	88.5	150—152 Toluene



Table 2 (Continued)

No.	R <sup>3</sup>	R <sup>2</sup>	Formula	M	Calculated/found			Yield %	M.p., °C Solvent
					% C	% H	% N		
<i>XLIX</i>	Cl	C <sub>6</sub> H <sub>5</sub>	C <sub>10</sub> H <sub>7</sub> ClN <sub>2</sub> O <sub>2</sub>	222.62	53.78	3.15	12.57	86.9	181—183 Butanone
					54.01	3.23	12.66		
<i>L</i>	CH <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>	218.20	60.34	4.57	12.82	65.8	179—181 Toluene
					60.12	4.40	12.52		
<i>LF<sup>f</sup></i>	CH <sub>3</sub> S	C <sub>6</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S	234.26	56.37	4.30	11.95	68.9	214—217 EtOH
					56.11	4.22	12.14		
<i>LII</i>	C <sub>2</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	232.22	61.95	5.13	12.04	43.8	140—143 Cyclohexane
					62.15	5.00	11.92		

a) % S 18.61/18.43; b) % S 17.17/17.19; c) % S 16.01/15.78; d) % S 12.57/12.44; e) % S 13.63/13.46; f) Ref. [2] 204—205°C.

adjusted to pH 7 with hydrochloric acid, cooled to 5°C and filtered, or chloroform (200 ml) was added. The compounds *XLI*, *XLIII*, and *XLVII*, present in the precipitate or in chloroform, were crystallized. The filtrate or the aqueous layer were acidified with hydrochloric acid and cooled to 5°C. The compounds *XX*, *XXII*, and *XXVII* were filtered off and crystallized.

### *Compounds XXIV, XXVI, and XLV*

To potassium hydroxide (0.25 mole) in water (100 ml) 2-methyl-4,5-dipropoxy-3(2*H*)-pyridazinone or 2-methyl-4,5-diisopropoxy-3(2*H*)-pyridazinone (0.1 mole) were added. The reaction mixture was transferred into a steel cylinder (content 250 ml). The hermetically closed cylinder with the reaction mixture was kept at 150°C for 16—40 hrs. The unchanged pyridazinone was extracted with benzene (100 ml). The aqueous layer was neutralized with hydrochloric acid and the compound *XLV* thus obtained was crystallized. The filtrate was acidified with hydrochloric acid giving the compounds *XXIV* and *XXVI*.

### *Compounds XXXII, XLII, XLIV, XLVI, XLVIII, and LI*

To alkali hydroxide (0.3 mole) dissolved in a mixture of water (40 ml) and ethylene glycol (80 ml) 2-substituted 4-chloro-5-alkylthio-3(2*H*)-pyridazinone or 2-phenyl-4,5-diethylthio-3(2*H*)-pyridazinone (0.14 mole) were added and the reaction mixture was stirred for 8 hrs at boiling. Then it was poured into water (400 ml) and after acidifying with hydrochloric acid the product was filtered and purified by crystallization.

### *Compounds XLI, XLIII, XLVII, L, and LII*

To sodium iodide (0.11 mole) in propanone, butanone or dimethylformamide (250 ml) 2-substituted 4,5-dialkoxy-3(2*H*)-pyridazinone (0.1 mole) was added and the reaction mixture was stirred for 8—40 hrs at 55—80°C. The precipitated sodium salt of 2-substituted 4-hydroxy-5-alkoxy-3(2*H*)-pyridazinone, after dissolving in water (100 ml) and acidifying with hydrochloric acid, gave the corresponding hydroxy derivative. When the amount of the precipitate was too small, propanone, butanone or dimethylformamide were distilled off *in vacuo*. The residue was extracted with water and, after acidifying, the extract yielded 2-substituted 4-hydroxy-5-alkoxy-3(2*H*)-pyridazinone.

### *Compounds XXXIX, XL, and XLIX*

To alkali hydroxide (0.2 mole) in water (100 ml) 2-methyl-4-alkoxy-5-halo-3(2*H*)-pyridazinone or 2-phenyl-4-alkoxy-5-halo-3(2*H*)-pyridazinone (0.1 mole) were added and the reaction mixture was stirred for 8 hrs at boiling. After addition of hydrochloric acid the product was filtered off and crystallized.

### *2-Methyl-4,5-dihydroxy-3(2H)-pyridazinone LIII*

Into 2-methyl-4,5-dimethoxy-3(2*H*)-pyridazinone (17 g) dry hydrogen chloride was introduced rising simultaneously the temperature up to 180°C. Then ethanol was added carefully and the mixture was boiled and filtered immediately. Yield 7.8 g, m.p. 284—288°C.

For  $C_7H_8N_2O_3$  (142.11) calculated: 42.23% C, 4.22% H, 19.70% N; found: 42.88% C, 4.66% H, 19.88% N.

## References

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