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Abstract

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δ-LACTONES AND δ-LACTAMS

SULFOCHLORINATION OF 5,6-DISUBSTITUTED PYRONES-2

(Presented by Academician A. N. Nesmeyanov, 23 VI 1960)

Sulfonation and sulfochlorination of pyrones-2 have not been described in the literature. In the present work, we have for the first time carried out the sulfochlorination of 5,6-disubstituted pyrones-2, the method for the synthesis of which had been developed by us earlier ([1,2]).

When pyrones-2 were heated with chlorosulfonic acid at 70–90°, crystalline sulfochlorides (I–IV) were obtained in yields of 30–50%:

$$[\text{5,6-fused pyrone-2}] \xrightarrow{HOSO_2Cl} [\text{3-sulfochloride of 5,6-fused pyrone-2}] \quad (I)$$

$$[\text{5-}R\text{-6-methylpyrone-2}] \xrightarrow{HOSO_2Cl} [\text{3-sulfochloride of 5-}R\text{-6-methylpyrone-2}]$$
$$R = CH_3\ (II), \quad C_3H_7\ (III), \quad C_4H_9\ (IV)$$

The sulfochlorides obtained contained the sulfochloride group, apparently, in position 3 of the pyrone ring, by analogy with bromopyrones (obtained by bromination of pyrones-2), for which the 3-position of the bromine atom was rigorously proved ([3,4]).

Along with sulfochlorides, in all cases sulfonic acids V–VII were isolated from the reaction mixture in the form of their barium salts (yields 5–12%, calculated on the starting pyrone-2).

Sulfochlorides I–III, on boiling with water, were converted into crystalline sulfonic acids in 50–62% yield (identical, by analysis of the barium salts, with the sulfonic acids isolated directly from the reaction mixture during sulfochlorination):

$$[\text{3-sulfochloride of 5,6-fused pyrone-2}] \xrightarrow{H_2O} [\text{3-sulfonic acid of 5,6-fused pyrone-2}] \quad (V)$$

$$\text{[3-sulfochloride of 5-}R\text{-6-methylpyrone-2]} \xrightarrow{H_2O} \text{[3-sulfonic acid of 5-}R\text{-6-methylpyrone-2]}$$
$$R = CH_3\ (VI), \quad C_3H_7\ (VII)$$

Sulfonic acids V–VII were characterized by crystalline toluidides.

Experimental Part

Preparation of sulfochlorides and sulfonic acids from pyrones-2. To freshly distilled chlorosulfonic acid (19.4 g; 0.167 mole), cooled with ice, pyrone-2 (5 g; 0.033 mole) was added in small portions with stirring, and the reaction mixture was heated at 70–90° for 2 hr; it was then cooled and poured onto ice. The crystalline sulfochloride that separated (if it separated as an oil, it was treated with cold water and left for an hour, after which it crystallized completely) was filtered off, washed with cold water, and, after drying in a desiccator, recrystallized from dry carbon tetrachloride. After separation of the sulfochloride, the aqueous solution was extracted with chloroform; from the chloroform solution, after drying and evaporation of the chloroform, an additional amount of sulfochloride was isolated. The reaction conditions, constants, yields, and analytical data for the sulfochlorides obtained (I–IV) are given in Table 1.

Table 1

Pyrone-2-sulfochlorides-3

Sulfochlorides	Reaction temperature, °C	Yield, %	M.p., °C	Found, % C	Found, % H	Formula	Calculated, % C	Calculated, % H
5,6-Cyclohexanopyrone-2-sulfochloride-3 (I)	85–90	50	97–98	43.83	43.66	3.77	3.73	$C_9H_9O_4SCl$	43.46	3.65
5,6-Dimethylpyrone-2-sulfochloride-3 (II)	70–75	39	81–85	37.56	37.62	3.05	3.13	$C_7H_7O_4SCl$	37.77	3.17

Sulfochlorides	Reaction temperature, °C	Yield, %	M.p., °C	Found, % C	Found, % H	Formula	Calculated, % C	Calculated, % H
6-Methyl-5-propylpyrone-2-sulfochloride-3 (III)	75–80	47	114–115	43.23	4.61	$C_9H_{11}O_4SCl$	43.12	4.42
6-Methyl-5-butylpyrone-2-sulfochloride-3 (IV)	75–80	30	58–59	44.99	4.85	$C_{10}H_{13}O_4SCl$	45.37	4.95

The aqueous solution remaining after extraction with chloroform was evaporated until hydrogen chloride had been completely removed and was neutralized with an excess of barium carbonate; the precipitate of barium sulfate was then filtered off, and the filtrate was evaporated to a volume of 1-2 ml. The barium salts of the corresponding sulfonic acids that separated on cooling were washed with alcohol, then with ether, and again dissolved in a minimum amount of water; the filtered solution was evaporated, and the barium salts obtained, after treatment with alcohol and ether, were dried in vacuo at 100° (4 hr). The yields of the barium salts of sulfonic acids V–VII were, respectively, 5.5; 7.0; and 12.6%. Their analyses are given below. Barium salt of sulfonic acid V–found, %: Ba 22.62; 22.74. $C_{18}H_{18}O_{10}S_2Ba$. Calculated, %: Ba 23.05.

Barium salt of sulfonic acid VI–found, %: Ba 25.45; 25.44. $C_{14}H_{14}O_{10}S_2Ba$. Calculated, %: Ba 25.25.

Barium salt of sulfonic acid VII–found, %: Ba 22.74; 22.80. $C_{18}H_{22}O_{10}S_2Ba$. Calculated, %: Ba 22.90.

Hydrolysis of pyrone-2-sulfochlorides-3. 1 g of sulfochloride and 5 ml of water were heated on a boiling water bath for 5 hr. The hot solution was filtered and carefully evaporated to a minimum volume. The crystalline sulfonic acids that separated on cooling were pressed on a porous plate and dried. 5,6-Cyclohexanopyrone-2-sulfonic acid-3 (V) crystallized with two molecules of water:

Found, %: C 40.69; 40.75; H 5.25; 5.02
$C_9H_{10}O_5S \cdot 2H_2O$. Calculated, %: C 40.59; H 5.3

On prolonged drying this sulfonic acid loses part of its water of crystallization.

$(C_9H_{10}O_5S)_2 \cdot H_2O$. Found, %: C 44.83; 44.66; H 4.74; 4.88
Calculated, %: C 45.19; H 4.62

Since sulfonic acid V crystallized with water, which was difficult to remove, sulfonic acid V, as well as VI and VII, were analyzed

Table 2

Pyrone-2-sulfonic acids-3

Sulfonic acids	M.p., °C	Yield, %	Found Ba in barium salts,* %	p-Toluidides of sulfonic acids: m.p., °C	p-Toluidides of sulfonic acids: found N, %	p-Toluidides of sulfonic acids: formula	p-Toluidides of sulfonic acids: calculated N, %
5,6-Cyclohexanopyrone-2-sulfonic acid-3 (V)	142–143 (from acetone)	57	23.43	247–248 (from alcohol)	4.25; 4.45	$C_{16}H_{17}NO_4S$	4.39
5,6-Dimethylpyrone-2-sulfonic acid-3 (VI)	132–133 (from a benzene–acetonitrile mixture)	50	25.43	251–252 (with decomp.; from aqueous alcohol)	4.83; 4.64	$C_{14}H_{15}NO_4S$	4.77

Sulfonic acids	M.p., °C	Yield, %	Found Ba in barium salts,* %	p-Toluidides of sulfonic acids: m.p., °C	p-Toluidides of sulfonic acids: found N, %	p-Toluidides of sulfonic acids: formula	p-Toluidides of sulfonic acids: calculated N, %
6-Methyl-5-propylpyridine-2-sulfonic acid-3 (VII)	135–136 (from a benzene–acetonitrile mixture; in a sealed capillary)	62**	22.73	242–243 (from alcohol)	4.30; 4.54	$C_{16}H_{19}NO_4S$	4.35

* Compare the data given above.
** Since acid VII is hygroscopic and liquefies in air, its yield is given for the preparation of the barium salt.

in the form of their barium salts. All the sulfonic acids obtained were characterized by their *p*-toluidides. The melting points of the sulfonic acids, their yields and the percentage content of barium in their barium salts, as well as the constants and analyses of the *p*-toluidides, are given in Table 2.

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REFERENCES

1. N. P. Shusherina, M. Yu. Lur' e, R. Ya. Levina, DAN, **109**, 117 (1956).
2. N. P. Shusherina, R. Ya. Levina, Z. S. Sidneko, M. Yu. Lur' e, ZhOKh, **29**, 403 (1959).
3. F. Feist, Ber., **26**, 747 (1893).
4. F. Feist, Ber., **34**, 1992 (1901).

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