REACTION OF SULFUR WITH ORGANIC COMPOUNDS

XIX. REACTION OF SULFUR WITH ETHERS AND ESTERS OF p-ISOPROPYLPHENOL*

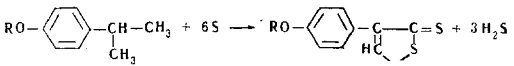
M. G. Voronkov and T. V. Lapina

UDC 547.738:542.945.22

Catalytic reaction of sulfur with the appropriate ethers and esters of p-isopropylphenol has given several previously unknown 4-p-alkoxyphenyl-, 4-p-aryloxyphenyl-, and 4-p-aroyloxyphenyl-1,2-dithiole-3-thiones.

The catalytic reaction of sulfur with alkylcumenes leads to the formation of the corresponding 4-alkylphenyl-1,2-dithiole-3-thiones [2-4]. This reaction is also successful when the aromatic cumene ring bears methoxy or ethoxy groups [4, 5].

We have shown that p-isopropylphenol, on heating with sulfur, undergoes complete resinification. However, many of its ethers and esters react smoothly with sulfur at 200-220° C in the presence of catalytic mercuriacetamide, according to the following scheme.

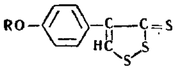


R = alkyl, aryl, aroyl

---

*For part XVIII, see [1].

TABLE 1. 4-(p-Hydroxyphenyl)-1,2-dithiole-3-thione and Its Ethers and Esters



R	Reaction conditions		mp, °C†	Molecular formula	Found, %			Calculated, %			Yield, %
	duration, hr	temp., °C			C	H	S	C	H	S	
H	—	—	179	$C_9H_6OS_3$	47,92	3,10	42.79	47.75	2.67	42.50	87.5
n-C_3H_7	4	214—216	134.2	$C_{12}H_{12}OS_3$	53.15	4.86	35.28	53,69	4.51	35.83	34.3
i-C_3H_7	5	217—219	144.3	$C_{12}H_{12}OS_3$	54.10	4.28	35.42	53.69	4,51	35,83	11.4
n-C_4H_9	3,5	218—220	132.8	$C_{13}H_{14}OS_3$	55,87	4.83	33,80	55,29	4.99	34.05	30.7
i-C_4H_9	6	212—214	143.5	$C_{13}H_{14}OS_3$	55,87	5.22	33.95	55.29	4,99	34.05	5.5
i-C_5H_{11}	6	215—217	142.3	$C_{14}H_{16}OS_3$	57.14	5.40	32,69	56.71	5.44	32,78	13.0
C_6H_5	4	217—220	118	$C_{15}H_{10}OS_3$	60,20	3.22	31,82	59.53	3.33	31.80	36.9
C_6H_5CO	4,5	214—216	168	$C_{16}H_{10}O_2S_3$	58.05	3.20	29.38	58.15	3.05	29.11	75.6

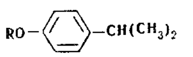
---

*In all cases, the molar proportions of the reagents $ROC_6H_4CH(CH_3)_2 : S$ were 1 : 1.5.

†After recrystallization from 80% ethanol.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 5, pp. 592-594, May, 1970. Original article submitted July 12, 1967.

TABLE 2. Esters and Ethers of p-Isopropylphenol



R	bp, °C (pressure, mm)	n_D^{20}	Yield, %
H	110—120 (25)	1,5237	72,0
n-C_3H_7	110—115 (15)	1,4952	65,0
i-C_3H_7	135—140 (40)	1,4905	55,0
n-C_4H_9	138—142 (15)	1,4932	78,0*
i-C_4H_9	152—156 (60)	1,4921	39,0
t-C_4H_9	151—154 (40)	1,5063	16,5
i-C_5H_{11}	168—172 (60)	1,4885	58,0
C_6H_5	149—155 (25)	1,5635	75,0*
$C_6H_5CH_2$	205—208 (45)	1,5505	58,5
CH_3CO	142—153 (50)	1,5058	41,5
C_6H_5CO	mp 65	—	26,0
$HOOCCH_2$	mp 101	—	29,0
$ClCH_2CH(OH)CH_2$	128—132 (2)	1,5220	30,5

---

*Obtained by alkylation of the corresponding phenyl ether (the other ethers and esters were obtained by the etherification or esterification of isopropylphenol). Esterification also gave 2-$C_6H_5COOC_6H_4$-$CH(CH_3)_2$, bp 195-200° C (50 mm), n_D^{20} 1.5268 (yield 41.5%), and 2-C_6H_5COO-4-$CH_3C_6H_3CH(CH_3)_2$, bp 210-212° C (25 mm), n_D^{20} 1.5518 (yield 92.0%).

Several 4-p-alkoxyphenyl-, 4-p-aryloxyphenyl-, and 4-p-aroyloxyphenyl-1,2-dithiole-3-thiones were synthesized in this manner (see Table 1). 4-p-Hydroxyphenyl-1,2-dithiole-3-thione itself was obtained by hydrolysis of 4-p-benzoyloxyphenyl-1,2-dithiole-3-thione, which proceeded much more readily than with the corresponding ethers (see the known method of synthesizing 5-p-hydroxyphenyl-1,2-dithiole-3-thione [6]). Sulfur did not react with o-benzoyloxycumene to any extent at 220° C, and in para-substituted t-butoxy-, benzyloxy-, and acetoxycumene gave only resinous reaction products. The reaction of sulfur with 1-chloro-3-(p-isopropylphenoxy)propan-2-ol and with p-isopropylphenoxyacetic acid gave similar results.

EXPERIMENTAL

The esters and ethers of p-isopropylphenol (Table 2) were obtained by the esterification or etherification of p-isopropylphenol, or by the alkylation of the corresponding phenol ethers with isopropanol in the presence of phosphoric acid [4]. In most cases, the para isomers were accompanied by traces of the ortho compounds. However, it was shown in separate experiments that, under the reaction conditions, the latter do not react with sulfur. Thus, in every case, only the ethers of 4-p-hydroxyphenyl-1,2-dithiole-3-thione were obtained. The solvent used for the reaction with sulfur, accompanied by traces of the corresponding o-isopropylphenyl ether and an excess of the para isomer, was o-dichlorobenzene, which was added in an amount sufficient to reduce the boiling point of the mixture to 210-220°C.

1-Chloro-3-(p-isopropylphenoxy)propan-2-ol was obtained by the condensation of p-isopropylphenol with epichlorohydrin in the presence of pyridine as catalyst [7].

p-Isopropylphenoxyacetic acid was prepared by the condensation of p-isopropylphenol with chloroacetic acid [8].

4-p-Propoxyphenyl-1,2-dithiole-3-thione. A 35.5 g (0.2 mole) quantity of p-n-propoxycumene, 10.0 g (0.31 g-at.) of sulfur, 0.1 g (0.0003 mole) of mercuriacetamide, and 2 ml of o-dichlorobenzene were heated under reflux at 214-216°C for 4 h. The reaction mixture was cooled, and the crystals which separated were drained and washed with a mixture of hexane and benzene (2 : 1). The yield of 4-p-n-propoxyphenyl-1,2-dithiole-3-thione was 4.8 g (34.3%), mp 134.2°C (from 80% ethanol). The other esters and ethers of 4-p-hydroxyphenyl-1,2-dithiole-3-thione were obtained in a similar manner (see Table 1).

4-p-Hydroxyphenyl-1,2-dithiole-3-thione. A solution of 2.0 g (0.006 mole) of 4-p-benzoyloxyphenyl-1,2-dithiole-3-thione in 70 ml of absolute ethanol saturated with HCl was heated to boiling for 1 hr. The cooled reaction mixture was diluted with water, and the crystals which separated were filtered off and recrystallized from 50% aqueous acetone to give 1.2 g (87.5%), mp 179° C.

LITERATURE CITED

1. M. G. Voronkov and V. E. Udre, KhGS [Chemistry of Heterocyclic Compounds], 452, 1970.
2. E. K. Fields, J. Amer. Chem. Soc., 77, 4255, 1955.
3. E. K. Fields, US pat. 2816075, 1957; C. A., 52, 7681, 1958.
4. M. G. Voronkov and T. V. Lapina, KhGS [Chemistry of Heterocyclic Compounds], 342, 1965.
5. M. G. Voronkov and T. V. Lapina, USSR patent no. 186,458, 1966; Byull. Izobr., no. 19, 29, 1966.
6. B. Böttcher and F. Bauer, Ber., 84, 458, 1951.
7. P. Spica, Gazz. chim. Ital., 10, 248, 1880.
8. W. Bergley, J. Forrest, and O. Stephenson, J. Chem. Soc., 1589, 1951.