[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Some New Sulfonic Acid Esters

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In the course of some other work in progress in this Laboratory it was necessary to prepare some benzene- and *p*-toluenesulfonic acid esters which had not been reported previously. In each case the three isomers have been characterized and the results are summarized in Table I and Table II.

were extracted with ether. The extracts were shaken successively with a 5% solution of potassium hydroxide, water, 5% hydrochloric acid and water. The ethereal solutions were dried with anhydrous sodium sulfate in the presence of norite. The mixtures were filtered, the ether

TABLE I

ESTERS OF BENZENESULFONIC ACID

Starting material	Solvent	Crystal form	Yield, %	M. p., °C.	Formula	Analyses, % Halogen Calcd.	Halogen Found	Sulfur Calcd.	Sulfur Found
o-Bromophenol	Methanol	Colorless platelets	90	54–56	$C_{12}H_9O_3BrS$	25.55	25.53[a]		
m-Bromophenol	(B. p. 217–218° at 10.5 mm.)		61		$C_{12}H_9O_3BrS$	25.55	25.78[a]		
p-Bromophenol	Petroleum ether[c]	Colorless needles	67	50–55[d]	$C_{12}H_9O_3BrS$	25.55	25.43[a]		
o-Phenylphenol	Dilute alcohol	Colorless needles	93	66–68	$C_{18}H_{14}O_3S$			10.32	10.34[a]
m-Phenylphenol	(B. p. 273° at 16 mm.)	Colorless solid	94	.....	$C_{18}H_{14}O_3S$			10.32	10.63[b]
p-Phenylphenol	Methanol[e]	Colorless needles	66	104–105	$C_{18}H_{14}O_3S$			10.32	10.63[a]

[a] Determinations made by the Carius method. [b] Determination made by the Parr bomb method. [c] Separated at about −82°. [d] The crude product boiled at 197–206° at a pressure of 2.5 mm [e] Final recrystallizations were from dilute ethyl alcohol.

TABLE II

ESTERS OF *p*-TOLUENESULFONIC ACID

Starting material	Solvent	Crystal form	Yield, %	M. p., °C.	Formula	Analyses, %[a] Halogen Calcd.	Halogen Found	Sulfur Calcd.	Sulfur Found
o-Bromophenol	Dil. alcohol	Colorless plates	98	77–79	$C_{13}H_{11}O_3BrS$	24.46	23.96		
m-Bromophenol	Methanol	Colorless rods	86	52–54	$C_{13}H_{11}O_3BrS$	24.46	24.46		
p-Bromophenol	Dil. alcohol	Colorless rectangular prisms	Quant.	93–95	$C_{13}H_{11}O_3BrS$	24.46	24.35		
o-Phenylphenol	Dil. alcohol; ligroin (68–70°)	Colorless needles	Quant.	64–66	$C_{19}H_{16}O_3S$			9.88	9.94
m-Phenylphenol	Methanol	Colorless cubes	90	52–54	$C_{19}H_{16}O_3S$			9.88	9.88
p-Phenylphenol	Alcohol:acetone = 1:1; benzene–ligroin (68–70°)	Colorless plates	75	178.5–179.5	$C_{19}H_{16}O_3S$			9.88	[b]

[a] These analyses were made by the Parr bomb method. [b] This compound was reported by Bell and Kenyon [*J. Chem. Soc.*, 3049 (1926)]. No yield was recorded; the reported m. p. was 177° for lustrous plates obtained from acetic acid.

To obtain these products the required acid chloride (1.1 mols) was added slowly with agitation to a pyridine solution of the phenol that was held at about 10°. Next the mixture was heated for half an hour at 60°, then gently refluxed for an equal period, cooled and treated with water and dilute hydrochloric acid. Products which separated as solids were collected by filtration; others distilled off, and the products allowed to solidify. The products obtained by either method were purified by crystallization from suitable solvents.

Summary

Some new esters of benzene- and *p*-toluenesulfonic acid have been prepared and their properties reported.

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