

[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		Sulfur	
						Calcd.	Found	Calcd.	Found
<i>o</i> -Bromophenol	Methanol	Colorless platelets	90	54-56	C ₁₂ H ₉ O ₃ BrS	25.55	25.53 ^a		
<i>m</i> -Bromophenol	(B. p. 217-218° at 10.5 mm.)		61		C ₁₂ H ₉ O ₃ BrS	25.55	25.78 ^a		
<i>p</i> -Bromophenol	Petroleum ether ^c	Colorless needles	67	50-55 ^d	C ₁₂ H ₉ O ₃ BrS	25.55	25.43 ^a		
<i>o</i> -Phenylphenol	Dilute alcohol	Colorless needles	93	66-68	C ₁₃ H ₁₁ O ₃ S			10.32	10.34 ^a
<i>m</i> -Phenylphenol	(B. p. 273° at 16 mm.)	Colorless solid	94	C ₁₃ H ₁₁ O ₃ S			10.32	10.63 ^b
<i>p</i> -Phenylphenol	Methanol ^e	Colorless needles	66	104-105	C ₁₃ H ₁₁ O ₃ S			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		Sulfur	
						Calcd.	Found	Calcd.	Found
<i>o</i> -Bromophenol	Dil. alcohol	Colorless plates	98	77-79	C ₁₃ H ₁₁ O ₃ BrS	24.46	23.96		
<i>m</i> -Bromophenol	Methanol	Colorless rods	86	52-54	C ₁₃ H ₁₁ O ₃ BrS	24.46	24.46		
<i>p</i> -Bromophenol	Dil. alcohol	Colorless rectangular prisms	Quant.	93-95	C ₁₃ H ₁₁ O ₃ BrS	24.46	24.35		
<i>o</i> -Phenylphenol	Dil. alcohol; ligroin (68-70°)	Colorless needles	Quant.	64-66	C ₁₃ H ₁₁ O ₃ S			9.88	9.94
<i>m</i> -Phenylphenol	Methanol	Colorless cubes	90	52-54	C ₁₃ H ₁₁ O ₃ S			9.88	9.88
<i>p</i> -Phenylphenol	Alcohol:acetone = 1:1; benzene-ligroin (68-70°)	Colorless plates	75	178.5-179.5	C ₁₃ H ₁₁ O ₃ S			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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