[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Some Derivatives of *s*-Triethylbenzene

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Mesitylene has been investigated thoroughly but its homolog, *s*-triethylbenzene, is comparatively little known; figures for its boiling point range from 200 to 220°. As the polyethylbenzenes are now readily available it seemed that this, the most abundant of the triethylbenzenes, merited further study.

Klages and Lickroth[2] found that *s*-triethylbenzene can be separated conveniently from its isomers by taking advantage of the facts that it is more difficult to sulfonate than its isomers and its sulfonic acid is hydrolyzed more readily. We have verified their observations and used their method for obtaining *s*-triethylbenzene from the proper fraction of the ethylation mixture.

The *s*-triethylbenzene used boiled at 211.2° at 760 mm. and had density 0.8772 0°/4° and 0.8568 25°/4°. The properties and analyses of the derivatives are given in Table I.

TABLE I

PROPERTIES AND ANALYSES OF DERIVATIVES OF *s*-TRIETHYLBENZENE

Name	B. p., °C.	Press.	M. p., °C.	d^0_4	d^{25}_4	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Sulfur Calcd.	Sulfur Found
s-Nitrotriethylbenzene	141.2	7	...	1.0550	1.0174	...	...	...	...	7.91	7.82	..	..
s-Triethylaniline	135.5	6	...	0.9492	0.9280	...	...	...	...	7.91	7.82	..	..
Acetyl derivative	...	..	149.5	....	....	76.65	76.63	9.65	9.54	..	..	..	..
Benzoyl derivative	...	..	181.3	....	....	...	...	...	...	..	..	..	..
s-Triethylthiocarbanilide	...	..	196.5	....	....	...	...	...	...	..	..	8.09	7.90
s-Triethylphenol[a]	126.5	5	...	.9716	.9504	80.84	80.91	10.18	10.08				
s-Triethylanisole	100.8	3	...	.9600	.9379	81.18	80.97	10.49	10.34	..	..	..	..
s-Triethylbenzonitrile	108.5	2	...	.9572	.9356								
Azo dye with β-naphthol	...	..	...	....	....	69.99	69.83	6.14	6.16				

[a] Since our work was done v. Auwers and Mauss, *Ann.*, **460**, 240 (1928), made this phenol by the reduction of 2,6-diethyl-4-acetylphenol and gave its b. p. as 244–246°.

Experimental

Into 200 g. (2.5 moles) of benzene and 50 g. of aluminum chloride 205 g. (7.4 moles) of ethylene was passed with stirring at 10,000 r. p. m. The temperature was about 60° at the start and was raised gradually to 85°. The absorption was slow at first but rose to 2500 cc. per minute. The products from several runs were fractionated and the fractions 190–230° united and refractionated. The triethylbenzene fraction was stirred for three hours at 60–70° with 2 parts of concentrated sulfuric acid. On cooling the mixture separated into 3 layers, the upper of which proved to be the desired *s*-triethylbenzene. The mixture of sulfonic acids was hydrolyzed by Armstrong's method.[3] At 110–125° the *s*-triethylbenzene was set free, while the liberation of the 1,2,4- did not occur until 160–175° was reached. The *s*-triethyl thus obtained was identical in all respects with the unsulfonated hydrocarbon above. This was proved by completely sulfonating a portion with 6 parts of sulfuric acid and converting the product into the amide which melted at 117–119°.[4]

It was nitrated with a mixture of 2 parts fuming to 3 concd. nitric acid at 25 to 30° for two hours which converts about half to the mononitro with a negligible amount of the dinitro which is obtained by stronger treatment. One part of the nitro derivative, 1 of water, and 3 of iron filings with a trace of acetic acid on the steam-bath for six hours gave the amino derivative which was purified by precipitation from benzene solution by hydrogen chloride. The acetyl and benzoyl derivatives were prepared by usual methods. The thiocarbanilide was prepared by adding 40% caustic soda solution to a cooled solution of the amine in carbon disulfide. The phenol was obtained through the diazo and methylated with dimethyl sulfate. The iodo derivative was made by the diazo. Its properties checked the data of Klages. It was converted into dichloride but this could not be isolated. The nitrile was obtained by the diazo reaction. The diazonium chloride was coupled with β-naphthol which gave a red azo dye.

Summary

A number of derivatives of *s*-triethylbenzene have been prepared and their properties determined.

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(1) Taken from Ph. D. dissertation of Winthrop B. Dillingham, Johns Hopkins University, June, 1926.

(2) Klages and Lickroth, *Ber.*, **32**, 1564 (1899).

(3) Armstrong, *J. Chem. Soc.*, **45**, 148 (1884).

(4) Klages[2] gives 118.5°.