

gives the best yield, though the method of Gladstone and Tribe may possibly be the most economical on account of the fact that the materials are cheaper. The crude product, however, is not nearly so pure as in case of that obtained by the first named method.

In 1895 Ullmann and Sponagle prepared phenyl ether by heating brom-benzene and phenol with finely divided copper as a catalyst. They thus increased the yield from .8 per cent to 87 per cent, according to their report. However, on going over their report we have found an error in their calculation and the yield should have been reported as 71 per cent of the brom-benzene employed.

We attempted to increase the yield of phenyl ether by the Ullmann-Sponagle method by using fused caustic potash and redistilled phenol to exclude as much water as possible. We also re-distilled the brom-benzene employed to insure its purity, since much of the brom-benzene on the market has been found to contain considerable di-brom-benzene. The reacting substances were heated in a Ladenburg flask for two hours, when the temperature rose to 230°, where it was maintained for about six hours, or until no phenol or brom-benzene passed over. The brom-benzene which distilled over was separated from the water which passed over with it and returned to the flask from time to time.

The phenyl ether was distilled over with steam and purified by distillation, when an almost white crystalline mass was obtained which boiled at 259-260°. An increase of 10 per cent was thus obtained and the product was distinctly superior.

The highest yield was 84.4 of the brom-benzene employed, while the highest yield using the stick caustic potash without fusion was 71.1 per cent.

Phenyl Ether Sulphonic Acid.—Hoffmeister (Ann. 159, 191) states that the mono-sulphonic acid derivative is formed along with the disulphonic acid derivative by treating phenyl ether with sulphuric acid, and that the former can readily be separated from the latter under suitable conditions, but he does not state what the conditions are, neither does he support his claim by any experimental data.

PHENYL ETHER AND SOME OF ITS DERIVATIVES

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A large number of methods have been devised for the preparation of phenyl ether, but most of them give very small yields. Two of the methods, however, give quite satisfactory yields. The method of Ullmann and Sponagle*

*Ber. 38, 2311.

We were unable to separate a mono-sulphonic acid or its barium salt from the di-derivative, although repeated attempts were made to do so by the method of fractional crystallization.

An attempt was therefore made to determine the effect of treating phenyl ether with varying proportions of concentrated and fuming sulphuric acid under varying degrees of temperature. In each case the barium salt was prepared by neutralizing the free acid with barium carbonate and analysis made for barium, without any effort to purify it.

Fuming sulphuric acid reacts very quickly without the aid of heat. Ordinary concentrated sulphuric acid requires the heat of a boiling water bath for several hours to effect a complete reaction. A sharp heat, however, will cause the two substances to combine in a very few minutes. The following results were obtained:

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| One volume of phenyl ether and one volume of concentrated sulphuric acid, heated on the water bath | 32.32% Ba. |
| One volume of phenyl ether and one volume of sulphuric acid, direct sharp heat | 30.08% Ba. |
| One volume of phenyl ether and four volumes of concentrated sulphuric acid, on boiling water bath | 28.83% Ba. |
| One volume of phenyl ether and one half volume of concentrated sulphuric acid, on water bath | 28.99% Ba. |
| One volume of phenyl ether and one volume of fuming sulphuric acid | 28.24% Ba. |
| One volume of phenyl ether and four volumes of fuming sulphuric acid | 29.92% Ba. |
| One volume of phenyl ether and four volumes of concentrated sulphuric acid, with sharp heat | 28.37% Ba. |
| One volume of phenyl ether and four volumes of concentrated sulphuric acid (method not recorded) | 31.20% Ba. |

Calculated Results

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| Barium in barium phenylether mono-sulphonate | 21.60% |
| Barium in barium phenylether di-sulphonate | 29.46% |
| Barium in barium phenylethertetrasulphonate | 36.3% |

Since a low heat, heating for a short time or heating with a large excess of phenyl ether, did not produce a com-

pound low in content of barium when changed to the barium salt, it does not seem that there is any tendency to form the mono-sulphonate of phenyl ether which Hoffmeister thought he had obtained.

Phenyl Ether Di-nitrile ($\text{CN.C}_6\text{H}_4\text{OC}_6\text{H}_4\text{.CN}$).—This substance was prepared by heating intimate mixtures of the sodium salt in phenyl ether di-sulphonic acid and potassium cyanide in a conical flask on a sand bath. The nitrile collected on the sides and in the neck of the flask in the form of glistening white flakes. The yield was very small. The substance is soluble in alcohol, ether acetone, benzene and xylene. It melts at $212^\circ\text{--}215^\circ\text{C}$. and turns yellow on exposure to light. It is readily saponified to the corresponding acid by dilute acids or alkalies. The composition was shown by the analysis of the silver salt of the acid.

Phenyl Ether Dicarboxylic Acid ($\text{COOH.C}_6\text{H}_4\text{OC}_6\text{H}_4\text{.COOH}$).—This was prepared by boiling the nitrile with dilute caustic potash. The transformation takes place with great readiness and the yield is quantitative. The acid was precipitated from the alkaline water solution after saponifying, with hydrochloric acid as a white powder. It was purified by crystallizing from hot water. It melts in the neighborhood of 230°C .

Silver Salt.—The silver salt was prepared from the acid by dissolving in dilute ammonia, evaporating off the excess, and precipitating with silver nitrate. It came down in curdy lumps, which blackened on exposure to light. An analysis yielded 45.11 per cent of silver. Theory requires 45.72 per cent.

Phenyl Ether Disulphon Chloride ($\text{ClSO}_2\text{.C}_6\text{H}_4\text{OC}_6\text{H}_4\text{.SO}_2\text{Cl}$).—This was prepared by intimately mixing the sodium sulphonate of phenyl ether and phosphorus pentachloride and heating on a rapidly boiling water bath for half an hour and pouring into ice cold water. The yield of the unpurified product was about 80 per cent of theory. The product was of a granular consistency, soluble in ether, acetone, carbon tetrachloride, and chloroform. It is rather stable toward some reagents. It is soluble in a solution of caustic soda on continued boiling, dissolves in alcohol with-

out odor of ether, with which it apparently does not react; is not soluble in water on long boiling to any notable extent. The water, however, acquires a slightly acid reaction, due no doubt to partial hydrolysis of the substance, though the reaction seems to be very slight.

Phenyl Ether Disulphon Amide ($\text{NH}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$).—This was prepared by fusing the sulphon chloride with ammonium chloride. It crystallizes well from a mixture of hot alcohol and water and melts at $179^\circ\text{-}180^\circ\text{C}$. Analysis for sulphur yielded the following results:

Found: (I) 19.61% S; (II), 19.21% S. Calculated, 19.52%. The Schotten-Bauman reaction takes place readily with phenol and aniline but the substances refused to crystallize from any of the solvents at hand.

An attempt was made to prepare the di-hydroxy derivative of phenyl ether by fusing the di-sodium sulphonate of phenyl ether with caustic potash. A reaction was obtained by adding the dry sodium sulphonate to fused caustic potash. A yellow, pasty mass was obtained which, on dissolving in water and adding sulphuric acid, evolved sulphur dioxide fumes copiously. On extracting with ether a brown mass, viscous when warm and brittle when cold, was obtained which we were unable to purify by crystallization but which yielded a distinct reaction for phenol with ferric chloride.

It was our purpose at the outset of this investigation to determine experimentally the orientation of the sulphonic acid group in the phenyl ether molecule, but our efforts in this regard were not crowned with success. Phenyl ether will not saponify by heating in a closed tube with caustic alkalies or hydrochloric acid. The attempt was made by Hoffmeister and repeated by ourselves several times without success. It was thought that the introduction of an acid group into each nucleus might reduce the stability of the molecule and it could be saponified, producing well known compounds, which could be readily identified. In the case of the dicarboxylic acid the yield was so small that no attempt could be satisfactorily made. In the case of the sulphonic acid it was found that it was

quite as stable as phenyl ether itself, and resisted all attempts to saponify it with caustic alkalies or hydrochloric acid when heated in a closed tube at high heat for a long time. On heating with nitric acid in a sealed tube, however, a quantitative yield of picric acid was obtained.

SUMMARY

1. Attention is called to the fact that there exists an error in the calculation of Ullmann and Sponagle with regard to the yield of phenyl ether in their published research.

2. By the use of anhydrous materials we have increased the yield in the method of Ullmann and Sponagle in the preparation of phenyl ether by 10 per cent on the average, with a maximum of 14.4 per cent in the highest result obtained.

3. We were able to obtain, under varying methods of procedure, only one sulphonic acid derivative of phenyl ether, notwithstanding the fact that Hoffmeister believed he had obtained two.

4. We were unable to hydrolyze the sulphonic acid derivative of phenyl ether by heating the substance in a closed tube with caustic alkalies or hydrochloric acid, indicating its great stability, like that of the mother substance. However, it is hydrolyzed by means of nitric acid under these conditions, but probably only after nitration has taken place, picric acid being the final result.

5. Several new derivatives of phenyl ether have been prepared and described.