

The senior author takes this opportunity of expressing his appreciation to Professor L. Charles Raiford of the University of Iowa under whose direction he first became interested in diphenyl. The present work has been continued with the kind permission of Professor Raiford.

### Summary

1. The chlorination of 4-hydroxydiphenyl using a number of solvents is described. The inves-

tigation of the trichloro derivative is continuing.

2. 3-Chloro-4-hydroxydiphenyl forms monobromo or dibromo derivatives depending somewhat upon the choice of solvents.

3. The chlorohydroxydiphenyls have been further characterized by the preparation of their 2,4-dinitrophenyl ethers and of the benzoates. 2,4-Dinitrochlorobenzene serves as a useful reagent in the preparation of phenolic derivatives.

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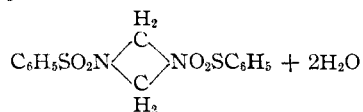
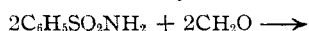
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

## Condensations of Some Toluenesulfonamides with Trioxymethylene and with Formaldehyde Solution

BY L. McMASTER

In 1893 Magnus-Levy<sup>1</sup> prepared, by the action of formaldehyde on benzenesulfonamide, a condensation product consisting of two isomeric substances,  $(C_7H_7SO_2N)_2$  and  $(C_7H_7SO_2N)_3$ . There was no evidence of the formation of a lower molecular weight compound. He concluded that the following reaction took place, forming di-benzenesulfon-di-methylene-di-imide



Tri-benzenesulfon-tri-methylene-tri-imide was formed at the same time.

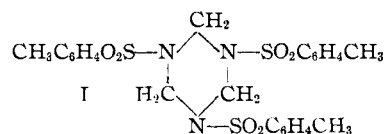
In 1922-23 Meister Lucius and Brünig<sup>2</sup> obtained patents on resinous substances resulting from the condensation of aromatic sulfonamides with 40% formaldehyde solution. In the first patent are described the results for *p*-toluenesulfonamide. Under various conditions several resinous substances were obtained having different properties with respect to solubility and hardness. A mixture of *o*- and *p*-toluenesulfonamide was condensed with formaldehyde, resulting in the formation of still different products. No statement is made of the composition or structure of the products formed. In one of the above patents, only mention is made of the possibility of using trioxymethylene in place of formaldehyde solution.

(1) Magnus-Levy, *Ber.*, **26**, 2148 (1893).

(2) *Farbwerke vorm. Meister Lucius and Brünig in Höchst a. M.*, German Patents 359,676 and 369,644.

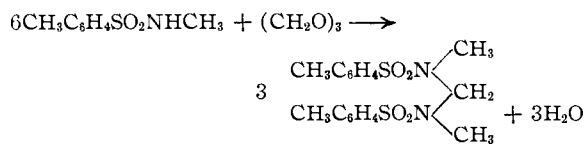
Since the product formed by the condensation of trioxymethylene and *p*-toluenesulfonamide is now manufactured for use as a plasticizer, it was suggested to us by the Monsanto Chemical Works to determine its composition and properties. I wish to thank this company for proposing this part of the work. I also wish to express my appreciation for the suggestions of Dr. Jules Bebie. The problem was then extended to include the *o*-compound and several alkyl derivatives of the para in order to study the course of the condensations and the properties of the compounds formed, not only when trioxymethylene but also when a 40% formaldehyde solution was used. I was assisted in portions of this work by Messrs. M. J. and C. W. Wiegand, R. S. Wobus and S. S. Cooper, to whom I extend my thanks.

Whereas Magnus-Levy obtained both the di- and tri-imides when benzenesulfonamide was condensed with 40% formaldehyde solution, we obtained by our methods only tri-*p*-toluenesulfon-tri-methylene-tri-imide or 1,3,5-tri-*p*-toluenesulfon-hexahydro-*sym*-triazine (Formula I) when trioxymethylene or 40% formaldehyde was used with *p*-toluenesulfonamide.



It was then decided to try the possibility of preparing a condensation product by the action of an

N-alkyl derivative of the *p*-amide with trioxymethylene and also with a 40% solution of formaldehyde. The same compound was formed in each case with the N-methyl derivative. No ring formation could take place here and the equation might be indicated as



This compound would have the empirical formula  $\text{C}_{17}\text{H}_{22}\text{N}_2\text{S}_2\text{O}_4$ ; however, analysis and mol. wt. determinations show  $\text{C}_{17}\text{H}_{24}\text{N}_2\text{S}_2\text{O}_5$ . We therefore believe that to each of the three molecules of condensate one molecule of water of crystallization is attached. That it is firmly held is proved by the fact that there was no loss in weight when the material was kept in a vacuum desiccator over concentrated sulfuric acid at 5 mm. for five hours. When placed in an oven at 108–110° for ten hours, a colorless, viscous liquid was formed with a loss of 11.5% in weight, presumably due to some decomposition, because after the material solidified the melting point was lowered about 4°.

With *o*-toluenesulfonamide, both the di- and tri-imides were easily prepared when trioxymethylene was used, but only the di-imide was formed with 40% formaldehyde solution.

## Experimental

### Condensations of *p*-Toluenesulfonamide

**With Trioxymethylene.**—Mixtures of 100 g. of the amide, 20 g. of trioxymethylene and 40 g. of glacial acetic acid were heated at 85–95° until a clear solution was obtained, which required from forty-five to sixty minutes. A mixture of 5 cc. of glacial acetic acid and 5 cc. of concentrated sulfuric acid was added slowly with constant stirring. The reaction mixture first became turbid and finally solidified. During this stage of the reaction the temperature was kept at 100°. The resulting mass was then baked on the steam cone for two hours. It was then broken up and washed twice by decantation with 100-cc. portions of boiling water. After the condensation product was disintegrated into a fine, white material, it was filtered off, washed with boiling water until acid free and then twice with 100-cc. portions of a 1% boiling sodium hydroxide solution to remove resinous material. It was dried at 90°; yields, 97–105 g. It crystallized from toluene as large crystals of m. p. 169.5°; from acetone, 169.8–170.5° (corr.).

A quantity of the condensate was prepared using a 30% excess of trioxymethylene and heating on an oil-bath at 120–125°. After addition of the sulfuric acetic acid mixture, the temperature of the bath was raised to 135° for about two hours. After being washed, dried and crys-

tallized from acetone, the material had a m. p. of 169.3°. A 20% less yield than in the first reaction was obtained.

The product is somewhat soluble in hot alcohol and very soluble in a boiling mixture of equal parts of alcohol and acetone from which it crystallizes in large orthorhombic crystals. It is readily soluble in aniline from which crystallizes a white compound of m. p. 73°, which decomposes on warming into aniline and the original product. This addition compound may also be decomposed by washing it a number of times with ether.

*Anal.* Calcd. for  $(\text{C}_8\text{H}_9\text{SO}_2\text{N})_x$ : C, 52.43; H, 4.96; N, 7.65; S, 17.50. Found: C, 52.72, 52.57; H, 5.21, 4.92, 4.96; N, 7.42, 7.44; S, 17.57, 17.56.

**Molecular Weight Determinations of the Condensate.**—These were determined mostly by the freezing point lowering of camphor, using the method of Rast.<sup>3</sup> The material crystallized from acetone gave 587 and 588 as the mol. wts. It should be 183 if  $x = 1$ . One set of determinations on a sample prepared by the Monsanto Chemical Works and crystallized from toluene gave an average of 539 while a second series of determinations on the same sample gave an average of 355.

Very recent determinations by S. S. Cooper gave 528 for the sample crystallized from acetone and 522 for the one from toluene. These figures were obtained by using the highest melting point of the mixture of the material and camphor. In each case it was noticed that, on cooling, the solid would become liquid again at a definite temperature, remain so for a few degrees, and then become solid. Heating from below this point the solid would melt sharply at the lower melting point, remain liquid over the same range as on cooling above, become solid and then melt sharply again. It thus appears that in the molecule  $x = 3$  but that the value of  $x$  changes during certain temperature ranges. Using phenol and diphenyl ether as solvents, factors of 2.5 to 3 were obtained. Boiling benzene gave similar results.

**With 40% Solution of Formaldehyde.**—Fifty-gram portions of *p*-toluenesulfonamide were dissolved in 200 cc. of alcohol to which 50 cc. of the formaldehyde and 3 cc. of concentrated hydrochloric acid were added. This solution was heated to dryness on the water-bath, yielding a very viscous mixture. This was then treated with the same quantities of alcohol, formaldehyde and hydrochloric acid, and the mixture again evaporated to dryness. The resulting viscous material was washed twice with 100-cc. portions of boiling 1% sodium hydroxide solution and then with water until neutral. The product was completely dissolved after four extractions with 50-cc. portions of hot alcohol. From each of the cold alcohol extracts the same material as that prepared with trioxymethylene was obtained; yields, approx. 40%. On acidifying the caustic soda washings considerable unchanged *p*-toluenesulfonamide was reclaimed.

### Condensations of *p*-Toluenesulfonmethyl and Ethyl Amides

**With Trioxymethylene.**—Fifteen grams of *p*-toluenesulfonmethylamide and 3 g. of trioxymethylene were heated with 10 cc. of glacial acetic acid for thirty minutes at 100° with stirring. Five cc. of the glacial acetic-

(3) Rast, *Ber.*, **55**, 1051 (1922).

sulfuric acid mixture was added to the solution, which was then heated at 100° for three hours with stirring. The mixture was then allowed to stand at room temperature for several days, during which time white crystalline plates separated. They were washed with hot 1% sodium hydroxide solution, then with water, and recrystallized from hot alcohol; m. p. 113–114° (corr.); yield, 9 g. Attempts to prepare the compound at temperatures ranging from 110 to 130° gave only a brown, gummy mass.

*Anal.* Calcd. for  $C_{17}H_{24}N_2S_2O_6$ : C, 50.97; H, 6.04; S, 16.00; N, 7.00. Found: C, 50.8; H, 6.08; S, 16.5; N, 6.92. *Mol. wt.* (Camphor). Calcd., 400. Found: 373.

In a similar manner it was attempted to bring about a condensation of the ethylamide with trioxymethylene but only a brown, viscous liquid was obtained.

**With 40% Solution of Formaldehyde.**—Ten grams of *p*-toluenesulfonmethylanide, 10 cc. of formaldehyde, 40 cc. of alcohol and 1 cc. of concentrated hydrochloric acid were heated in an evaporating dish upon the steam cone. A sticky mass resulted. Formaldehyde, alcohol and acid were again added and the mixture evaporated a second time. The resulting material was washed several times with hot 1% sodium hydroxide solution and then with boiling water. The pale yellow residue was dissolved in hot alcohol and recrystallized several times. White plates of m. p. 113–114° were obtained; yield, 4 g. They proved to be identical with the compound made when trioxymethylene was used.

With the ethyl amide a small quantity of pale yellow crystals of m. p. 104–105° was obtained, most of the unchanged amide being recovered from the sodium hydroxide washings.

#### Condensations of *o*-Toluenesulfonamide

**With Trioxymethylene.**—The procedure was approximately the same as with the *p*-amide. One hundred grams gave a yield of 96 g. of white crystals. After recrystallization from xylene the product melted at 245.5–246.5° (corr.) with slight decomposition.

*Anal.* Calcd. for  $(C_8H_9SO_2N)_x$  as in the case of the *p*-compound. Found: C, 52.54; H, 4.92; N, 7.44; S, 17.26. *Mol. wt.* (Camphor). Calcd.,  $(183)_x$ . Found: 553, 558;  $x = 3$ .

The compound is partially soluble in alcohol, only slightly soluble in toluene, fairly soluble in xylene and extremely so in aniline. As in the case of the *p*-condensate a white addition product of m. p. 259.2–259.4° (corr.) crystallizes from the aniline. It decomposes on standing.

The method was now modified slightly by the addition of water to the reaction mixture. Fifty grams of *o*-toluenesulfonamide, 10 g. of trioxymethylene, 25 g. of glacial acetic acid and 50 cc. of water were mixed, heated and condensed as above. A heavy, viscous layer insoluble in

the dilute acid formed. This was separated by decantation, digested with hot alcohol and the mixture filtered. A white solid remained, which, after washing with alcohol, drying, and recrystallization from xylene, melted at 168.8–169.9° (corr.) without decomposition: yield, 7.4 g.

*Anal.* Calcd. for  $(C_8H_9SO_2N)_x$ . Found: C, 51.8; H, 4.91; N, 7.39; S, 17.85. *Mol. wt.* (Camphor). Calcd.,  $(183)_x$ . Found: 327;  $x = 2$ .

The filtrate was evaporated on the steam-bath and a viscous, sticky material remained. This was digested with 150 cc. of *N* sodium hydroxide solution at 95°. A white precipitate was filtered off, washed with hot water and alcohol, and dried at 90°; yield, 11 g.; m. p. 243° without purification, indicating that it was the tri-imide.

**With 40% Solution of Formaldehyde.**—Fifty grams of *o*-toluenesulfonamide, 50 cc. of formaldehyde, 150 cc. of alcohol and 5 cc. of concentrated hydrochloric acid were mixed and evaporated on the water-bath. This procedure was repeated. The resulting viscous, sticky material was digested with two 100-cc. portions of hot *N* sodium hydroxide solution, whereupon a white solid formed. This product was filtered, washed with water and dried; yield, 17 g.; m. p. 241–243°, which approximates that of the product obtained when trioxymethylene was used. Unchanged amide was recovered from the filtrate.

#### Summary

Condensations of *o*- and *p*-toluenesulfonamides with trioxymethylene and with 40% formaldehyde solution have been found to take place with the formation of C–N ring compounds, similar in structure to those found when benzenesulfonamide is condensed with 40% formaldehyde. The *o*-amide gave both the di- and tri-imides with trioxymethylene; with the formaldehyde solution, only the tri compound resulted. Only the tri-imide was prepared with the *p*-amide; no attempt was made to prepare the di-imide.

*p*-Toluenesulfonmethylanide gave a condensation product with both the trioxymethylene and the formaldehyde solution. It is not a C–N ring compound and presumably possesses the structure indicated with one molecule of water of crystallization. The corresponding ethylamide gave no definite results.

Some of the properties of the condensation products are recorded. The tri-imides form addition compounds with aniline.

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