

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE.]

THE TOLYL ESTERS AND TOLUIDIDES OF THE NITROSULFONIC ACIDS OF *p*-XYLENE.

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In an earlier paper, by Karslake and Huston,¹ three nitrosulfonic acids of *p*-xylene were described. These were prepared by the nitration of *p*-xylenesulfonic acid, or the sulfonation by means of chlorosulfonic acid of nitro-*p*-xylene. Separation of the products was effected by fractional crystallization of the sulfonchlorides from ether and petroleum ether. The configuration was determined by reducing the free acids to the corresponding aminosulfonic acids.

In addition to those described in the previous paper, the following derivatives of the three nitrosulfonic acids of *p*-xylene have been prepared: The *o*-, *m*- and *p*-tolyl esters and the *o*- and *p*-toluidides. A description of these follows.

Preparation of the Tolly Esters.—The crude sulfonchlorides were repeatedly recrystallized until they melted sharply at their respective melting points. The tolyl esters were then prepared as follows:²

0.75 g. of purified cresol (*o*-, *m*-, or *p*-) was mixed in a glass-stoppered bottle with 1 g. of pyridine, 1.75 g. of the purified sulfonchloride was then added. Heat was evolved. The mixture was placed in a constant temperature oven at 90° for fifteen minutes. After standing over night at room temperature, it was washed repeatedly with cold water. The ester was then dissolved in hot alcohol and set aside to crystallize.

Preparation of Toluidides.—The following method was used in the preparation of all of the toluidides:

1.5 g. of the purified sulfonchloride was dissolved in 20 cc. of carbon tetrachloride and treated with an excess (2 cc.) of freshly distilled toluidine (*o*- or *p*-). The solvent was evaporated off on the water bath. The residue was washed repeatedly with 10% hydrochloric acid and dissolved in 5% sodium hydroxide³ solution. After filtering, the toluidide was precipitated with dilute hydrochloric acid, washed and recrystallized, first from 95% alcohol and then from 50% alcohol, until pure.

Derivatives of 6-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

***o*-Tolly Ester**, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.—The sulfonchloride dissolved readily in the pyridine-cresol solution, and crystals began to form at once. After washing and recrystallizing four times from alcohol, the ester melted sharply at 66–67° (corr.). It forms nodules of opaque,

¹ THIS JOURNAL, 36, 1244 (1914).

² Ber., 35, 1443 (1902).

³ All the toluidides studied are partially decomposed by 10% sodium hydroxide.

flat, pointed crystals, fairly soluble in alcohol, ether, chloroform, carbon tetrachloride and benzene, only slightly soluble in petroleum ether, and insoluble in water.

Subst.: 0.3566 g.; cc. 0.1 *N* HCl, 10.9. Calc.: N, 4.36%. Found: N, 4.28%.

The Gunning-Jodlbauer modification of the Kjeldahl method was used.

***m*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.—The sulfonyl chloride dissolved more slowly in the pyridine-*m*-cresol mixture than it did in the pyridine-*o*-cresol mixture.

The ester is much less soluble in organic solvents than the *o*-tolyl ester and slightly more soluble than the *p*-tolyl ester. It comes down from alcoholic solution in well-formed rhombohedral plates which melt at $71.5-72^\circ$ (corr.).

Subst.: 0.4191 g.; cc. 0.1 *N* HCl, 12.9. Calc.: N, 4.36%. Found: N, 4.31%.

***p*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.—This ester is the least soluble in organic solvents of the tolyl esters of the 6-nitrosulfonic acid. It crystallized from alcohol in clusters of very thin, lustrous plates which melt at $93.5-94.5^\circ$ (corr.).

Subst.: 0.3158 g.; cc. 0.1 *N* HCl, 9.8. Calc.: N, 4.36%. Found: N, 4.35%.

***o*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—This compound comes down from ninety-five per cent. alcohol in colorless plates and from fifty per cent. alcohol in clusters of very fine, flat needles. It is readily soluble in alcohol, chloroform, carbon tetrachloride, and benzene, less soluble in ether and petroleum ether; but insoluble in water. M. p. $126.5-127.5^\circ$ (corr.).

Subst.: 0.2587 g.; cc. 0.1 *N* HCl, 15.9. Calc.: N, 8.75%. Found: N, 8.61%.

***p*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—This is less soluble in organic solvents than the *o*-toluidide of the same acid. It began to precipitate immediately from the reacting mixture. It comes down from fifty per cent. alcohol in clusters of long, silky, colorless filaments. M. p. $135-136^\circ$ (corr.).

Subst.: 0.2807 g., 0.3476 g.; cc. 0.1 *N* HCl, 17.1, 21.5.

Calc.: N, 8.75%. Found: N, 8.53%, 8.68%.

Derivatives of 3-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

***o*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.—The sulfonyl chloride dissolved more slowly in the pyridine-*o*-cresol mixture than did either of its isomers. The mixture darkened when heated to 90° , but solidified immediately on cooling. This is the least soluble in organic solvents of the tolyl esters of the 3-nitrosulfonic acid. It crystallizes from alcohol in hard, opaque prisms which melt sharply at $151.5-152^\circ$ (corr.).

Subst.: 0.3743 g.; cc. 0.1 *N* HCl, 11.55. Calc.: N, 4.36%. Found: N, 4.29%.

***m*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.—The sulfonyl chloride dissolved a little more rapidly in the pyridine-*m*-cresol mixture than in the pyridine-*o*-cresol mixture. The ester comes down from alcohol in lustrous,

colorless plates. It is slightly more soluble than the *o*-tolyl ester of the same acid. M. p. 107.5–108° (corr.).

Subst.: 0.2989 g.; cc. 0.1 *N* HCl, 9.1. Calc.: N, 4.36%. Found: N, 4.27%.

***p*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.—The sulfonchloride dissolved readily. The reacting mixture did not completely solidify on standing over night. It was washed repeatedly with cold water until it solidified. This ester is much more soluble in organic solvents than the other tolyl esters of the same acid. On evaporation of its alcoholic solution at room temperature it tended to form an oily deposit. Crystallization is best carried on at about 10°. It comes down in fine, poorly formed, needle-like plates which melt after ten recrystallizations at 76–77° (corr.).

Subst.: 0.3128 g.; cc. 0.1 *N* HCl, 9.6. Calc.: N, 4.36%. Found: N, 4.3%.

***o*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—This compound is slightly more soluble in organic solvents than the *p*-toluidide of the same acid. It comes down from 50% alcohol in fine, lustrous, rhombohedral plates. M. p. 143.5–145° (corr.).

Subst.: 0.2638 g.; cc. 0.1 *N* HCl, 16.3. Calc.: N, 8.75%. Found: N, 8.65%.

***p*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—A heavy precipitate was formed immediately on the addition of the *p*-toluidine to the solution of sulfonchloride. The toluidide has about the same solubility in organic solvents as the *o*-toluidide of the 6-nitro acid. Crystallized from fifty per cent. alcohol it forms long, flat, lustrous needles which melt sharply at 158.5–159° (corr.).

Subst.: 0.2611 g., 0.2125 g.; cc. 0.1 *N* HCl, 16.1, 13.1.

Calc.: N, 8.75%. Found: N, 8.63%, 8.64%.

Derivatives of 5-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

***o*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.—This ester is much less soluble in organic solvents than the *o*-tolyl ester of the 6-nitro acid, and of about the same solubility as the *o*-tolyl ester of the 3-nitro acid. It crystallizes from alcohol in long (4 cm.), flat, opaque, soft needles which have a constant melting point of 99–100° (corr.).

Subst.: 0.3676 g.; cc. 0.1 *N* HCl, 11.3. Calc.: N, 4.36%. Found: N, 4.31%.

***m*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.—This is less soluble than the *o*-tolyl ester of the same acid and but slightly more soluble than the *p*-tolyl ester. It forms clusters of fine, flat, lustrous, brittle needles. M. p. 110–111° (corr.).

Subst.: 0.3179 g.; cc. 0.1 *N* HCl, 10.0. Calc.: N, 4.36%. Found: N, 4.40%.

***p*-Tolyl Ester**, $C_6H_2(CH_3)_2NO_2SO_3C_6H_4CH_3$.—This is the least soluble in organic solvents of any of the tolyl esters. It crystallizes from alcohol in long (5 cm.), lustrous, needle-like plates which melt at 117.5–118.5° (corr.).

Subst.: 0.3214 g.; cc. 0.1 *N* HCl, 10.2. Calc.: N, 4.36%. Found: N, 4.42%.

***o*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—This compound crystallizes from fifty per cent. alcohol in lustrous plates which retain a slight yellow color after repeated recrystallization. It is a little more soluble in organic solvents than the *p*-toluidide of the same acid. M. p. 140.5–141° (corr.).

Subst.: 0.2855 g., 0.2681 g.; cc. 0.1 *N* HCl, 17, 16.6.

Calc.: N, 8.75%. Found: N, 8.34%, 8.67%.

***p*-Toluidide**, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_4CH_3$.—It is the least soluble in organic solvents of the toluidides studied. It crystallizes in lustrous elongated plates which melt at 143.5–144.5° (corr.).

Subst.: 0.2783 g.; cc. 0.1 *N* HCl, 17.1. Calc.: N, 8.75%. Found: N, 8.61%.

Summary and Discussion.

A comparison of the melting points of tolyl esters of the nitrosulfonic acids of *p*-xylene reveals some peculiarities which are worthy of note, in the light of existing theories. The tolyl esters of the 5-nitro and 6-nitro acids follow the rule of symmetry, *i. e.*, the melting points increase from ortho to meta to para. The melting points of the tolyl esters of the 3-nitro acid, on the other hand, *decrease* from ortho to meta to para. This is especially peculiar in the light of a theory advanced by Smiles,¹ which assigns the lowering of fusion point to intramolecular collision. An examination of the structural formula of the *o*-tolyl ester of the 3-nitro acid shows that the substituting groups are in the most compact arrangement possible, while the melting point is higher than that of any of the other tolyl esters studied, *i. e.*, 151°. No record of esters of similar structure could be found in the literature.

The toluidides are more regular as regards their melting points. The *p*-toluidide of each acid melts at a higher temperature than the *o*-toluidide.

For any given acid the solubility of its derivatives in organic solvents decreases as the melting point increases.

As a rule the derivatives of the 5-nitro acid are less soluble than the derivatives of its isomers.

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THE ACTION OF DIPHENYLUREACHLORIDE ON ORGANIC BASES.

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Michler² first prepared diphenylureachloride by treating diphenylamine with phosgene in chloroform solution. Its action on ammonia

¹ "Relation between Chemical Constitution and Some Physical Properties," p. 208.

² *Ber.*, 8, 1665 (1875); 9, 396 (1876); see also Girard and Wilm, *Bull. soc. chim.*, 25, 251 (1901); Erdmann and Herth, *J. prakt. Chem.*, [2] 56, 6 (1897); melts at 189°.