Syntheses of Nitro-compounds by means of Oxidation of Acylamino-compounds. (I)

Synthesis of Nitro-benzenesulfonamide By The Odidation of Acetyl amino-benzene sulfonamide With Hydrogen Peroxide

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Margaret K. Seikel and the present auther[2] had studied the oxidation of sulfanilamide with hydrogen peroxide.

The present author applied this oxidation procedure to acetylaminobenzene sulfonamide, and found that acetylaminobenzene sulfonamide is oxidized to nitrobenzene sulfonamide.

Acetylaminobenzene sulfonamide was oxidized with hydrogen peroxide in glacial acetic acid and became to develop braun and then yellow colors. As the reaction solution was cooled, no marerial precipitated, in spite of the fact that acetylamino benzene sulonamide precipitates from the solution of such the concentration as this. This indicates that acethylamino-sulonamide was converted to unknown compounds.

The reaction solution was evaporated to almost dryness in vacum. Crystalization of the residues yielded crystals whose melting points was not sharp except that of crystalls (m. p. 156.5°) which was obtained from the reaction solution heated for 7 hours.

To remove the acetylamino benzenesulfonamide remaing unreacted, the residues were hydrolized with hydrochloric acid and the substance insoluble in hydrochloric acid were filtered. Recrystalizations from water yielded the yellow needles which melted at 178°. This substance did not lower the melting point of an authentic nitrobenzenesulfonamide.

From the acidic solution, removed of nitrobenzene sulfonamide, sulfanilamide (m.p. 162°) was recovered. This did not lower the melting point of an authentic sample.

From the facts mentioned above it is concluded that the reaction solution was the mixture of acetylaminobenzene-sulonamide and p-nitobenzene sulfonamide. This mixture was very soluble in water, even though both acetylamino- and nitro-benzenesulfoamide were sparingly soluble in water.

It seems probable that both compound formed eutectic mixture which was soluble in water. This was confirmed by the thermal analysis.

Nitro- and acetylamino-benzenesulfonamide formed eutectic mixture in the molecular ratio of 2 to 1.

There are many literatures, dealing with the preparation of nitro compounds, but the present procedure of synthetizing nitro-compounds by means of the oxidation of acetylamino compound may be a new method for many kinds of acetylamino compounds.

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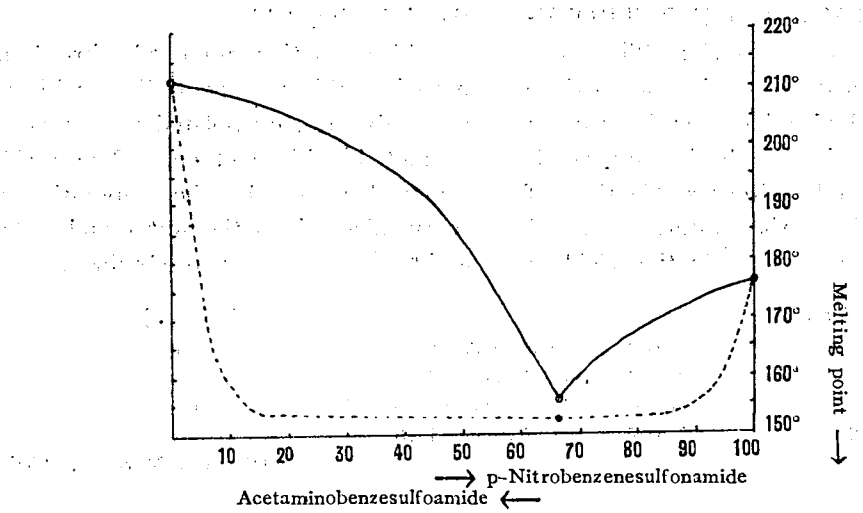
2) This Annual Report.



Summary

1) Acetylamino benzene sulfonamide is oxidized with hydrogen peroxide in glacial acetic acid to yield nitro benzene sulofnamide in fair yield.

2) Nitro- and acetylamino-benzene sulfonamide formed eutectic mixture in the molecular ratio of 2 to 1.

Expeimental

Formation of Eutectic Mixture Between Acetylamino benzene sulofnamide and Nitrobenzene sulfonamide.

Acetylaminobenzene sulfonamide (mg.)	Nitrobenzene sulfonamide(mg.)	Mol. ratio	Imbibition point	melting point
85	15		153°	203.2°
70	30		〃	195.5°
52	40.4		〃	187°
42.8	40.4	1 : 1	〃	176°
42.8	50		〃	170.2°
42.8	60.6	2 : 3	〃	167.5°
42.8	70		〃	161.5°
42.8	80.8	1 : 2	〃	156.5°
42.8	90		〃	160.5°
15	85		〃	169.5°

OXIDATION PROCEDURE : The mixture of 6.25g. of acetylaminobenzenesulfonamide, 120cc. of glacial aceticacid and 30cc. of 30% hydrogenperoxide was heated on the water bath for 2—12 house. By the evaporation to dryness in vacum yellow materials were obtained. Recrystallization from the water produced the mixture of acetylamino- and nitro-benzenesulfonamide in the yield of the following table.

Time for heating	Yields	Melting point
2 hours	6.1g.	
7	5.9	156.5°
12	5.7	

PREPARATION OF NITROBENZENESULFONAMIDE : The mixture which was dissolved in 15cc. of 10 % pottasiüm hydroxide was heated on the water bath for one half hours, acidified and filtrated. Recrystallization of the residues from the water, produced yellow needle, mp. 178° in the yield of the following table.

The solution removed nitro benzenesulfonamide was neutralized with sodium carbonate, evapolated to dryness and extracted with acetone. The residues removed acetone by the evaporation, was recrystllized from the water and sulfanilamide (mp. 162°) was obtained.

Time for heating		Yields (%)
2 hours	Nitrobenzenesulfonamide 0.8g.	13.55%
7 〃	Nitrobenzenesulfonamide 1.54	51.5
	Acetylaminobenzenesulfonamide 0.65	27.0
12 〃	Nitrobenzenesulfoaamide 1.75	56.5

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