Summary

6-Methyltetralin, prepared by the catalytic hydrogenation of β-methylnaphthalene, is substituted in the 7-position in the Friedel and Crafts reaction with phthalic anhydride. The resulting keto acid has been used as the starting material for the synthesis of the 4-methyl and the 4,9- and 4,10-dimethyl derivatives of 1,2-benzanthracene, as well as their 1′,2′,3′,4′-tetrahydro derivatives, all of which are of interest in investigating the relationship between structure and carcinogenic activity. Although the syntheses were completed successfully, some difficulty was experienced in the dehydrogenations, apparently because of the ease of elimination of meso alkyl groups.

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Separation of Sulfuric Acid from Nitric, Alkyl- and Arylsulfonic, and Alkylsulfuric Acids by Means of Liquid Ammonia

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The ammonium salts of many oxy acids such as sulfuric, phosphoric, oxalic and arsenic are insoluble in liquid ammonia. Use has been made of the insolubility of some of these ammonium salts in liquid ammonia to effect the preparation of such nitrogen bases as hydrazine,[1] semicarbazide[2] and hydroxylamine[2] by ammonolysis of the respective sulfates, oxalates, phosphates and arsenates. The nitrogen bases are very soluble in liquid ammonia and are recovered in the anhydrous condition by evaporation of the solvent.

This marked insolubility of ammonium sulfate in liquid ammonia suggested that liquid ammonia might be used for the removal of excess sulfuric acid where the latter is employed either by itself or with other reagents. The experimental results reported in this paper demonstrate that it is possible (1) to separate quantitatively sulfuric and nitric acids by conversion into the ammonium salts and extraction of soluble ammonium nitrate with liquid ammonia; (2) to use liquid ammonia as a solvent for alkyl- and arylsulfonic acids, as well as alkylsulfuric acids; (3) to use liquid ammonia for the removal of excess sulfuric acid from compounds of the types listed under (2), especially where it is desired to produce directly the ammonium salts of the alkyl- and arylsulfonic acids and alkylsulfuric acids.

Experimental

It should be emphasized that no special apparatus is necessary in using liquid ammonia for the reactions outlined below. Filtration is carried out using ordinary Büchner funnels and filter flasks. It is a simple task to cool the funnel and flask quickly by running a small quantity of liquid ammonia through the filter. Filtration is simplified where sintered glass crucibles or filter funnels are used in place of filter paper. Naturally, good ventilation is not only desirable, but necessary.

Separation of Sulfuric Acid from Nitric Acid.—The separation and recovery of nitric and sulfuric acids in the spent acids after use in nitration reactions, by conversion into ammonium salts and extraction with liquid ammonia is practically quantitative. In a typical experiment a solution containing 20.8 g. of 96% sulfuric acid and an approximately equal quantity of concentrated nitric acid was neutralized with concentrated aqueous ammonia. The solution was evaporated and the solid residue treated with 200 cc. of liquid ammonia. The insoluble ammonium sulfate was removed by filtration, washed with liquid ammonia, heated at 60°[3] for several hours and weighed; yield, 26.8 g. of ammonium sulfate corresponding to a 99.3% recovery. No sulfate was found to be present in the ammonium nitrate recovered from the filtrate.

Solubility of Alkyl- and Arylsulfonic Acids and Alkylsulfuric Acids in Liquid Ammonia at −33°.—A representative number of compounds of this type were prepared and their solubility in liquid ammonia tested qualitatively. With the exception of laurylsulfuric acid, all compounds listed below are readily and easily soluble to the extent of at least 10 g. in 100 cc. of ammonia. Solution of these acids in liquid ammonia brings about their conversion into the ammonium salts. In a number of cases the products obtained upon evaporation of the liquid ammonia solution were recrystallized from absolute alcohol and analyzed for their nitrogen content. These compounds are listed in Table I.

In extending this study to other derivatives of these acids, it was found that the sodium salts of benzenesulfonic acid and *n*-butylsulfonic acid are very soluble in liquid ammonia, whereas the sodium salts of laurylsulfuric and benzylsulfonic acids are only slightly soluble.

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[1] Browne and Welsh, THIS JOURNAL, **33**, 1728 (1911).

[2] Audrieth, *ibid.*, **52**, 1250 (1930).

[3] Heating is necessary due to the fact that ammonium sulfate forms a number of ammonates which must be decomposed to obtain the anammonous salt.

TABLE I

Ammonium salts of acids	Mol. formula	Analysis, % N Calcd.	Found
Sulfanilic	$C_6H_{10}O_3N_2S \cdot {}^1/_2H_2O$	14.28	14.22
Benzenesulfonic	$C_6H_9O_3NS$	8.00	7.84
o-Aminobenzenesulfonic	$C_6H_{10}O_3N_2S \cdot {}^1/_2H_2O$	14.28	14.15
p-Toluenesulfonic	$C_6H_{11}O_3NS$	7.41	7.35
2-Aminotoluene-5-sulfonic	$C_7H_{12}O_3N_2S$	13.72	13.65
Naphthionic	$C_{10}H_{12}O_3N_2S$	11.66	11.36
d-Camphorsulfonic	$C_{10}H_{19}O_4NS$	5.62	5.54
o-Nitrobenzenesulfonic	$C_6H_8O_5N_2S$	12.67	12.49
m-Nitrobenzenesulfonic	$C_6H_8O_5N_2S$	12.67	12.78
p-Nitrobenzenesulfonic	$C_6H_8O_5N_2S$	12.67	12.77
β-Naphthalenesulfonic	$C_{10}H_{11}O_3NS$	6.22	6.07
Laurylsulfuric	$C_{12}H_{29}O_3NS$	4.94	5.07

Ammonium Ethyl Sulfate.—A mixture of 50 g. of sulfuric acid (96%) and 70 g. of ethanol was refluxed for two and one-half hours on the steam-bath. The reaction mixture was then saturated with gaseous ammonia and the excess of alcohol removed by evaporation. The solid residue was treated with 200 cc. of liquid ammonia, allowed to stand for one hour and the ammonia insoluble material removed by filtration, weight of ammonium sulfate recovered 32.2 g., corresponding to 23.9 g. of pure sulfuric acid. Evaporation of the filtrate yielded 28.6 g. of $C_2H_5OSO_3NH_4$, approximately 90% of the theoretical yield based upon the sulfuric acid which had reacted.

Ammonium Lauryl Sulfate.—Nineteen and two-tenths grams of lauryl alcohol in 40 cc. of ether was treated with 19 g. of concentrated sulfuric acid (96%) and allowed to stand at room temperature for forty-eight hours. After removal of the excess ether, the residual liquid was treated directly with gaseous ammonia, resulting in the formation of a solid mass. This mixture was digested for one hour with 400 cc. of liquid ammonia. Filtration and evaporation of the liquid ammonia solution yielded 10 g. of a white crystalline product possessing excellent detergent properties. This material was recrystallized from alcohol and washed with ether. Analysis showed this compound to be the ammonium salt of laurylsulfuric acid. The yield obtained corresponds to a 34% conversion of the alcohol into the ammonium salt. The ammonia-insoluble residue was found to contain unreacted alcohol, ammonium sulfate and some ammonium lauryl sulfate. Qualitative tests indicate that the solubility of ammonium lauryl sulfate is greater than 5 g. but less than 10 g. per 100 cc. of liquid ammonia at −33°. The solubility increases markedly, however, with rise in temperature.

Ammonium Sulfanilate.—Twenty-eight grams of aniline and 80 g. of concd. sulfuric acid were heated at 180–190° for five hours. The solid product was neutralized with aqueous ammonia and the resulting solution evaporated until the total volume of solid and liquid had been reduced to approximately 100 cc. The material was treated directly with 400 cc. of liquid ammonia, allowed to digest for one hour and filtered. Evaporation of the filtrate and subsequent drying of the product in a vacuum desiccator yielded 41.5 g. of the ammonium sulfanilate, $H_2NC_6H_4SO_3NH_4$, corresponding to a 72% yield based on the aniline used. The product was sulfate free, indicating that removal of ammonium sulfate is possible even in the presence of considerable quantities of water.

Sodium and Ammonium Benzene Sulfonates.—Two 20-g. samples of benzene were converted into benzenesulfonic acid by treatment with 83.3 g. of fuming sulfuric acid (15% SO_3). One sample was neutralized in the cold with aqueous sodium hydroxide, the other with aqueous ammonia. The solutions were concentrated on a steam-bath to a sirupy consistency and each digested with 400 cc. of liquid ammonia. Removal of the ammonium sulfate and evaporation of the liquid ammonia filtrate gave in the first experiment 42.1 g. of sodium benzene sulfonate (91%) and in the other case 41.1 g. of the ammonium salt (91.5%). The above values are those obtained after the removal of diphenyl sulfone, which is soluble to a limited extent in liquid ammonia.

Summary

It has been demonstrated experimentally that liquid ammonia permits the quantitative removal of sulfuric acid as ammonium sulfate from mixtures containing nitric acid, alkyl- and arylsulfonic acids or alkylsulfuric acids.

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