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STUDIES IN DIPYRIDYL CHEMISTRY. VII*. SULFUR TRIOXIDE SULFONATION OF γ,γ'-DIPYRIDYL

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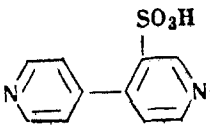
Reaction of γ,γ'-dipyridyl with sulfur trioxide at room temperature gives γ,γ'-dipyridyldisulfotrioxide, which latter on heating at 200° gives γ,γ'-dipyridyl-sulfonic acid. Salts of γ,γ'-dipyridyl-3-sulfonic acid are prepared, among them the potassium, sodium, barium, and 3-cyano-γ,γ'-dipyridyl salts.

Previous work [1, 2] was concerned with a study of the sulfonation of γ,γ'-dipyridyl with sulfuric acid. The present paper gives results regarding the sulfonation of γ,γ'-dipyridyl with sulfur trioxide at room temperature under conditions used in preparing pyridinesulfotrioxide [3]. Reaction was effected by mixing dichloroethane solutions of sulfur trioxide and γ,γ'-dipyridyl (2:1) and gave γ,γ'-dipyridyldisulfotrioxide, a crystalline substance which unlike the starting base is insoluble in alcohol but soluble in water.

Heating γ,γ'-dipyridyldisulfotrioxide at 200° gave (unlike pyridinesulfotrioxide, which is unchanged under such conditions) γ,γ'-dipyridyl-3-sulfonic acid (I), isolated as its barium salt. The potassium and sodium salts are prepared from the barium salt by exchange reactions. (I) was obtained in the free state by the action of an equimolecular amount of sulfuric acid on the barium salt.

The position of the sulfonic acid group was determined by melting the potassium salt with potassium ferricyanide, when the resultant nitrile was found to be identical with 3-cyano-γ,γ'-dipyridyl, previously prepared (by the present authors) from γ,γ'-dipyridyl-3, 5, 3', 5'-tetrasulfonic acid.

Thus the structural formula of I can be:



I

EXPERIMENTAL

γ,γ'-Dipyridyldisulfotrioxide. 20 g γ,γ'-dipyridyl in 50 ml dry dichloroethane are poured, with cooling, into a solution of 40 g crystalline sulfur trioxide in 200 ml of the same solvent. The precipitate is filtered off, washed with dichloroethane, and dried in a vacuum desiccator. M.p. 201-202° (from alcohol). The sulfo group is estimated by precipitation with barium chloride.

γ,γ'-Dipyridyl-3-sulfonic acid (I). 5 g γ,γ'-dipyridyldisulfotrioxide are heated for 3 hr at 200° in a round-bottomed flask on a sandbath. After cooling, the reaction mixture is dissolved in water and treated with barium carbonate (until neutral or slightly alkaline to litmus). The precipitate of barium sulfate and carbonate is filtered off, the filtrate taken to dryness and treated with alcohol, at which time a crystalline precipitate is obtained. It is filtered off, washed with alcohol, yielding 0.5 g (5.2%) of the barium salt of I. On standing, γ,γ'-dipyridyl separates from the mother liquor.

The barium salt of I is a white crystalline substance, rather easily soluble in water, insoluble in alcohol and acetone. For analysis the barium salt was dried at 100° (1-2 mm). Found: Ba 23.83; 22.66; 22.70%. Calculated for $C_{20}H_{14}N_4O_6S_2Ba$: Ba 22.84%.

The calculated amount of sulfuric acid is added to 1 g barium salt of I and dissolved in hot water. The resultant precipitate of barium sulfate is filtered off and the filtrate taken to small volume on a steam bath. On standing colorless crystals of I begin to separate. The acid is insoluble in alcohol, but soluble in water. For analysis the acid was dried at 100° (1-2 mm). Found: equiv. 233.69; 234.15. Calculated for $C_{10}H_8N_2O_3S$: equiv. 236.00.

The potassium salt of I is prepared by adding an equimolecular quantity of potassium carbonate to a solution of the barium salt; the filtrate is evaporated, after removing the barium carbonate, and alcohol added to the residue. On standing the potassium salt of I crystallizes out from the alcoholic solution. This salt is pale rose-colored and soluble in water, but insoluble in alcohol. Found: K 14.11; 14.07, 14.12%. Calculated for $C_{10}H_7N_2O_3SK$: K 14.23%.

*For Part VI see [1].

The sodium salt of I is prepared in the same way as the potassium salt and is recrystallized from hot alcohol. It is a white crystalline substance, readily soluble in water, difficultly soluble in alcohol. For analysis it is dried at 100° (1-2 mm). Found: Na 8.72, 8.88, 9.04%. Calculated for $C_{10}H_7N_2O_3SNa$: Na 8.91%.

3-Cyano-γ,γ'-dipyridyl. 2 g potassium salt of I are mixed with 6 g potassium ferricyanide and heated in a retort on a sandbath, when an oil distils over and solidifies in the neck of the retort. Recrystallization from toluene gives a substance with m.p. 152-153°, undepressed (m.p. 151-152°) on admixture with 3-cyano-γ,γ'-dipyridyl. Found: N 22.08; 22.78%. Calculated for $C_{11}H_7N_3$: N 23.20%.

REFERENCES

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