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Tetsuji Kametani and Kunio Ogasawara: An Improved Synthesis of Styphnic Acid.

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Styphnic acid, namely, 2,4,6-trinitroresorcinol (2,4-dihydroxy-1,3,5-trinitrobenzene) (Ⅲ) had been prepared industrially for example, by first sulfonating and then nitrating resocinol.[1,2] This paper provides a less expensive and more efficient process for the production of styphnic acid in high yield on an industrial scale.

The purpose of the present investigation has been achieved by the provision of the process for the preparation of styphnic acid which comprises warming an aqueous mixture of 2,4-dinitrosoresorcinol (Ⅱ) and nitric acid and recovering the styphnic acid so produced. A preferred experiment of this research is the process for the preparation of Ⅲ which comprises the consecutive steps of adding sulfuric acid to a cooled, aqueous solution of resorcinol (I), sodium hydroxide and sodium nitrite to produce 2,4-dinitrosoresorcinol, recovering the 2,4-dinitrosoresorcinol and then warming a mixture of the above compound (Ⅱ) and nitric acid to produce styphnic acid.

The process of the present research is represented by the following reaction scheme:

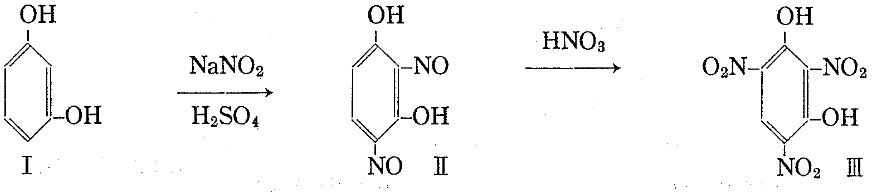

Chart 1.

Experimental

2,4-Dinitrosoresorcinol (II)——Crystalline $NaNO_2$ (7.0 g.) was gradually added to a pale clear blue solution of 5.5 g. of resorcinol (I) in a mixture of 2.4 g. of NaOH and 100 ml. of water which was cooled to less than 0° and vigorously stirred. To the above mixture was added dropwise 54 ml. of sulfuric acid (d: 1.32). During the first addition of 10 ml. of H_2SO_4, the reaction temperature rose severely. Therefore, a suitable amount of ice was added in order to prevent the temperature from rising vigorously. The mixture became pale brown and yellow crystals began to separate. After all of the H_2SO_4 solution had been added during 1.5 hr. and the mixture had been stirred for an additional one hour, the crystalline product, 2,4-dinitrosoresorcinol, was collected by filtration and washed fully with ice-water. Recrystallization from dilute EtOH gave the compound (Ⅱ) as a yellowish brown powder (8 g., 95%), m.p. 158°, which was used without much purification in the following reaction because of its instability. Both Liebermann and potassium iodide reaction were positive.

Styphnic Acid (III)——To a cooled and stirred suspension of 100 g. of 2,4-dinitrosoresorcinol (Ⅱ) in 600 ml. of water there was added a solution of 700 g. of HNO_3 (d: 1.38) in 300 ml. of water. The mixture was heated on a water-bath, and evolution of a reddish-brown gas was observed. After the above suspension had become clear and the severe reaction ceased, yellow crystals of the product separated. Collection of the product by filtration and recrystallization from benzene afforded the styphnic acid (Ⅲ) (120 g., 81.5%) as pale yellow cubes, m.p. 175~176°, whose infrared spectrum was superimposable on that of an authentic sample. *Anal.* Calcd. for $C_6H_3O_7N_3 \cdot H_2O$: C, 29.40; H, 1.23. Found: C, 29.18; H, 1.58.

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