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An Improved Method of Synthesis of 2,6-Dinitrobromobenzene

by

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An Improved Method of Synthesis of 2,6-Dinitrobromobenzene

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A better method for synthesis of 2,6–dinitrobromobenzene both in respect of procedure and yield, has been develoed

INTRODUCTION

Although there are several publications on the syntehesis of 2,6– dinitrochlorobenzene, a few work exist on its analoguous, 2,6–dinitrobromobenzene. Welsch [1] dissolved 2,6–dinitroani-treated with curpous chloride and obtained 2,6–dinitrochlorobenzene. Gunstone and Tucker [2] used sulfuric acid and acetic acid as solvent for 2,6–dinitroaniline, diazotized and treated with curprous chloride and optained the same compound (both are the Sandmeyer reaction). Borsche [3] dinitrated chlorobenzene and treated so formed mixture with sodium ethylacetoacetate. Thus, 2,4– dinitrochlorobenzene did give a reaction with it but 2,6–dinitrochlorobenzene did not, and extracted with ether from reaction mixture. Körner [4] dissolved 2,6–dinitroaniline in nitric acid and diazotized, treated with cuprous chloride or bromide and obtained 2,6–dinitrochloro bromobenzene. There was no mention about the yield. However, verification of the reaction for 2,6–dinitrobromobenzene gave low yield. Parker and Read [5] has prepared 2,6–dinitrochloro / and bromobenzene for some reactions without giving the details of the preparations. Hodgson and Walker [6] dissolved 2,6–dinitroaniline in glacial acetic acid and diazotized with cold mixture of sodium nitrite in conc. sulfuric acid. It is reported that, precipipitation of 2,6-dinitroaniline sulfate in this reaction affected the rate of diazotization. On the other hand cuprous chloride or bromide solution are added immediately into the diazonium salt solution. In this manner, dimerization of aryl radicals which has already been observed in the similar reactions, has been prevented.

In the present work, both Gunston and Tucker's and Hudgson and Walker's work have been considered and a modified method has been developed and much higher yield has been reached.

Starting material, 2,6–dinitroaniline was made according to Welsch [1]. and Gunstone and Tucker [2] and Schultz [8], via suldonation of chlorobenzene, dinitration of so formed 4–chlorobenzene sulfunic acid, amination of, 3,5–dinitro-4–chlorobenzene sulfonic acid to 2,6–dinitroaniline.

EXPERIMENTAL

Solution (*A*). In a 100 ml three neck round bottom flask which was equipped with a mechanical stirrer, a dropping funnel and a themomerter, was set on an ice bath. Into the flask was introduced 75 g of conc. sulfuric acid (d = 1.84) and cooled down to nearly O °C., then 4.0 g (58 mmoles) of finely grounded sodium nitrite was put in the cold sulfuric acid in small portions while continuous stirring. Into this mixture, 9.0 g (50 mmoles) of 2,6–dinitroaniline in 100 ml warm glacial acetic acid was added slowly while continuous stirring. Temperature of the mixture in the flask should not exceed 40 °C. A limpid solution was formed at the end of the reaction.

Solution (*B*). Into a 250 ml erlenmayer flask was put 80 ml of conc. hydrobromic acid (d = 1.49) and 14.2 g (50 mmoles) of cuprous bromide and heated up to get a clear but slightlyly coloured solution. In order to discharge its color a little copper bronze (very fine copper powder) was added into the hot solution, then flask was stoppered and cooled down to room temperature.

Colution (A) (diazonium solution) was porured immediaately into the solution (B) and mixed thoroughly. It let stand for about 2 hours until nitrogen evolution was stopped, then heated up to 80 °C. Homogenious material was poured in a 250–300 ml ice cold water. So formed precipitate was filtered out by means of a Büchner funnel, washed with 50 ml of saturated sodium carbonate solution then with 100 ml of water. Crude product was dried in a vacuum dessicator overnight. Crude and dry material was dissolved in 100 ml of warm benzene, shaked with conc. sulfuric acid (three times, each 5 ml), dried over anhydrous sodium sulfate, evaporated down to about 20 ml, into this contentrated solution, 50–60 ml of light pertoleum (b.p. 90–140 °C) was added, heated over 80 °C, then let stand to crystallize. Solid crystalline material was filtered and dried, 6.6 g (30 mmoles) of product (yield 60 %) was obtained. Melting poind is 106–106.5 °C (uncorr.), pale green long needles. After recrystallization from cyclohexane, melting point rised to 107 °C. (Reported value is 107 °C [4])

In order to transform it to 2,6–dinitroaniline, small amount of material was treated with conc. ammonia, so formed substance crytallized from ethanol and melted at 139 °C., (Reported 139 °C [2]). No depression was observed melting point an admixture of this material and an authentic sample.

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ÖZET

Bu makalede, 2,6–dinitrobrom benzen elde etmek için, şimdiye kadar mevcut olan metodlardan hem işlem hem de verim bakımından daha uygun bir metodun geliştirildiği açıklanmıştır.

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