

Short Communications

A Novel Synthesis of 1-Bromo-3,5-dinitrobenzene

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1-Bromo-3,5-dinitrobenzene was first prepared by Elion¹. His method involved bromination of 2,4-dinitroaniline to 2-bromo-4,6-dinitroaniline. The amine group was then replaced with hydrogen by diazotisation and reduction with ethanol. The substance was later prepared by Derbyshire and Waters², who simply brominated *m*-dinitrobenzene in conc. sulphuric acid solution containing silver sulphate. The bromide ions resulting from the heterolysis of bromine were continually removed as insoluble silver bromide. Thus, the concentration of bromonium ion could be maintained at a level necessary for the reaction to proceed at a reasonable rate.

The present author wishes to report that 1-bromo-3,5-dinitrobenzene may be prepared in good yield by the Hunsdiecker reaction between silver 3,5-dinitrobenzoate and bromine in carbon tetrachloride solution at reflux temperature under anhydrous conditions. The synthesis is a simple extension of the work by Barnes and Prochaska³, who found that the silver salts of the three isomeric nitrobenzoic acids all give good yields of the corresponding bromonitrobenzenes. It is interesting to note that the introduction of a second nitro group has practically no influence upon the reaction rate. This supports the generally accepted homolytic mechanism rather than a heterolytic one. Furthermore, the product formed is the expected one. The danger of forming the *m*-dinitrobenzene, owing to the decarboxylation of the 3,5-dinitrobenzoate ion, could not *a priori* be overlooked. However, there seem to be no complications of this kind.

Experimental. Silver 3,5-dinitrobenzoate. The preparation of this salt was carried out as described in the literature.⁴ Starting with equimolecular quantities of 3,5-dinitrobenzoic acid (Fluka) and silver nitrate, a 94 % yield of the silver salt was secured. In order to obtain a perfectly dry product, at least two days' storage at 70°C was found necessary.

1-Bromo-3,5-dinitrobenzene. A solution of 65.2 g (0.408 mole) bromine in 100 ml carbon tetrachloride was added during one hour to a vigorously stirred, refluxing mixture of 127.4 g (0.400 mole) silver 3,5-dinitrobenzoate and 500 ml carbon tetrachloride. The stirring and refluxing was then continued for 6 h. During this time, the evolution of carbon dioxide (generated in the reaction) gradually ceased. The course of the reaction could also be followed by the gradual disappearance of the intense bromine colour in the reaction mixture. The carbon tetrachloride solution was then filtered under suction through a sintered glass funnel. The filter cake, consisting of silver bromide, was thoroughly washed with carbon tetrachloride, and the combined filtrate and washings were shaken with sodium bisulphite solution until free from bromine. Acidic substances possibly present were then removed by washing three times with sodium carbonate solution. The carbon tetrachloride solution was finally washed with water until neutral and dried over calcium chloride. The solvent was distilled off at normal pressure, the last traces *in vacuo*, whereupon the remainder suddenly solidified to a yellowish, crystalline mass, melting at 74–75°C (on a Kofler Hot Stage apparatus). The crude product weighed 84.7 g, representing a yield of 86 %. One recrystallization from ligroin raised the melting point to 77°C, reported 77¹, 77–78². No depression of the melting point was observed upon admixture with an authentic sample of 1-bromo-3,5-dinitrobenzene, prepared according to Derbyshire and Waters.² Yield of recrystallized product 62.3 g or 63 %.

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Replacement of Bromine and Chlorine in 2-Halo-5-nitrobenzenediazonium Compounds by Chloride Ion

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In a recently published paper¹, the present author reported that nucleophilic halogen exchange reactions take place at room temperature between bromine or chlorine in 4-halo-3-nitrobenzenediazonium ion and chloride ion. Analogous reactions have now been found to take place between bromine and chlorine in 2-halo-5-nitrobenzenediazonium ion and chloride ion.

A kinetic investigation of these reactions is in progress, and some preliminary results will be presented below.

As far as possible, the competitive technique is applied, which means that at least two reactions are studied in the same kinetic run. This makes a safer comparison between their specific reaction rates possible, since the medium effects cancel. For further information about the experimental conditions, reference should be made to previous work.¹ It should be remarked that instead of the infrared spectroscopic technique employed earlier, quantitative gas chromatography has been adopted as the method of assaying the mixtures of dihalo-nitrobenzenes resulting from the kinetic experiments, since the latter method is considerably faster and has also been found to make possible the quantitative assay of a four-component mixture consisting of two isomeric pairs. Thus, competitive runs with 4-bromo-3-nitrobenzenediazonium ion and 2-bromo-5-nitrobenzenediazonium ion

in a large excess of chloride ion have been made.

The competitive runs with the two isomeric bromonitrobenzenediazonium ions and chloride ion mentioned in the previous paragraph were carried out at two different temperatures. At 25°C, the ratio between the rate constants for the 4-bromo-3-nitro isomer and the 2-bromo-5-nitro isomer was found to be 1.32, and at 15°C, the same ratio was 1.61. (An extrapolation in an Arrhenius plot gives the ratio 1.00 at 40°C.)

Figures for the corresponding exchange reactions between ³⁶Cl-labelled chlorine compounds and non-radioactive chloride ion cannot easily be obtained from competitive runs for experimental reasons but may be calculated indirectly. At 25°C, the ratio for the corresponding chlorine compounds is 1.0. No value at 15°C has been obtained as yet.

Finally, the ratio between the specific reaction rates for 2-bromo-5-nitrobenzenediazonium ion and 2-chloro-5-nitrobenzenediazonium ion in the reactions with chloride ion at 25°C has been found to be 2.02. This further confirms the two-step mechanism postulated¹ for these reactions, with the absence of an "element effect". The very close agreement with the ideal value 2 is, however, fortuitous, because experiments which are in progress indicate that the reactions have different temperature coefficients.

One more conclusion may be drawn from the data presented above. Structurally, the 2-halo-5-nitrobenzenediazonium ions may be imagined to arise from the 4-halo-3-nitrobenzenediazonium ions by letting the diazonium group and the nitro group change places. It is interesting to note that this reversal does not have any substantial influence upon the halogen exchange reaction rate constants, since a diazonium group and a nitro group might be expected to interact to a different extent with a large halogen atom like bromine in an *ortho* position, in virtue of their different steric requirements. It is quite probable that solvation of the charged diazonium group makes it "larger" in the thermodynamic sense than would be apparent from the inspection of a molecular model.

Actually, the similarity of the specific reaction rates for the different isomers is nothing but a confirmation of an empirical multiple-substitution-additivity rule for the free-energy-of-activation changes due to substitution. Reference should be made to a review of this subject by Joffé.²