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The Mechanism of the Nitrodeiodination of 2-Iodo-1,3,5-trineopentylbenzene

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When 2-iodo-1,3,5-trineopentylbenzene is nitrated in nitromethane with 90 % nitric acid, it undergoes nitrodeprotonation, as well as nitrodeiodination. The latter reaction was found to be a direct substitution of the iodine atom by a nitro group in analogy with the mechanism of the former reaction.

Results concerning the reaction between various alkyl-substituted iodobenzenes and fuming nitric acid in nitromethane were presented in a previous publication.[1] Two different reactions occurred with substrates having a hydrogen, as well as an iodine, atom attached to the benzene nucleus. These reactions were the usual nitrodeprotonation and a reaction in which the iodine atom is exchanged for a nitro group. The latter reaction was thought to be a direct nitrodeiodination.

Butler and Sanderson [2] showed recently that for the reaction between nitric acid and 4-iodoanisole in acetic acid, the observed nitrodeiodination takes place *via* an initial nitrosodeiodination and a subsequent oxidation. In Ref. 1, that mechanism was rejected for alkyl-substituted iodobenzenes since the rate of nitrodeiodination was not reduced when urea had been added to the reaction solution. As pointed out by Butler and Sanderson, such an experiment may not be completely conclusive and the dependence of the rate of nitrodeiodination on addition of nitrate may give more accurate information.

The present paper deals with the reaction between fuming nitric acid and 2-iodo-1,3,5-trineopentylbenzene (ITNB) in nitromethane solution, and evidence is presented for the view that the observed nitrodeiodination is a direct one.

ITNB was treated in nitromethane with 90 % nitric acid which was prepared with particular attention paid to minimizing the content of lower nitrogen oxides. The two products obtained were 2-iodo-1,3,5-trineopentyl-4-nitrobenzene (INO_2TNB) and 1,3,5-trineopentyl-2-nitrobenzene (NO_2TNB), resulting from nitrodeprotonation and nitrodeiodination, respectively.

From the composition of the product mixture, a quantity a was calculated; a is defined as twice the amount of NO_2TNB divided by the amount of INO_2TNB. In Ref. 1, it was reported that the value of a did not change during the course of reaction, and this result has been confirmed in the present work. It can thus be concluded that the value of a represents the ratio between the rates per available position of nitrodeiodination and nitrodeprotonation. The reaction was repeated several times with different amounts of sodium nitrite added to the reaction solution, and the value of a was determined in each case (see Table 1).

The a values increase with increasing molar ratio between added nitrite and ITNB, and a fairly good linear correlation can be found. The slope of the line is small, however, and the increase in a over the entire interval studied is less than half the value without addition of nitrite.

The observed nitrodeiodination could not be the result of a nitrosodeiodination followed by an oxidation because of the relatively high value of a in the case in which no nitrite was added and the small value of the slope of the correlation

Table 1. Nitration of 2-iodo-1,3,5-trineopentylbenzene (ITNB) with an excess of nitric acid containing varying amounts of sodium nitrite. For conditions, see Experimental section. The quantity a is defined as twice the ratio between the amounts of 1,3,5-trineopentyl-2-nitrobenzene and 2-iodo-1,3,5-trineopentyl-4-nitrobenzene.

mol $NaNO_2$ / mol ITNB	mol $NaNO_2$ / mol HNO_3	a
0	0	0.56
1.2	0.001	0.57
3.4	0.004	0.60
6.6	0.007	0.62
10.5	0.012	0.66
12.0	0.013	0.66
18.7	0.021	0.71
26.5	0.030	0.82
30.9	0.034	0.82

line. If this were the case, the nitric acid itself would have contained 7 mol % of nitrous acid, as can be found by extrapolation. The nitric acid prepared was not found to contain any detectable amounts of nitrous acid, within an experimental accuracy of 1 mol %.

The small increase in the a value observed when nitrite was added may be due to nitrodeiodination *via* a nitrosodeiodination, or to relative rate differences caused by medium effects. Neither of these possibilities can be ruled out.

The possibility that a catalytic effect of nitrite on the rate of nitrodeiodination may be hidden by a similar effect on the rate of nitrodeprotonation can be ruled out by means of the results from an estimate of the rate constants. In fact, the overall reaction rate decreased when sodium nitrite was added; see Experimental section.

A possible reaction sequence consisting of a protodeiodination followed by a nitrodeprotonation, leading to an overall nitrodeiodination has been ruled out.[1,3]

The reason for a difference between the mechanism found in the present case and that in the case of 4-iodoanisole may to some extent be rationalized in the following way. Butler and Sanderson [2] found a very low *ortho*:*para* ratio for the nitrosodeiodination reaction. Since the iodine in ITNB is placed between two *ortho* substituents the nitrosodeiodination may be hampered in this case, and the direct nitrodeiodination becomes the dominating path for the replacement of iodine by the nitro group.

EXPERIMENTAL

The NMR analyses were performed on a Varian A 60 NMR spectrometer. Gas chromatographic (GLC) analyses were made on a Perkin-Elmer 900 instrument fitted with SE-30 columns.

2-Iodo-1,3,5-trineopentylbenzene (ITNB) was prepared according to a method previously described.[3] The fuming nitric acid used was obtained according to Bennett *et al.*[4] The concentration was adjusted to 90 % by mixing with a proper amount of concentrated nitric acid. The acid was finally tested for nitrous acid according to a method based on reaction with *N*-chloro-4-toluenesulphonamide, described by Bennett *et al.*[4] No nitrous acid could be detected within the experimental accuracy of 1 mol %.

Nitration of ITNB with nitric acid. ITNB (100 mg, 0.24 mmol) was dissolved in 65 ml of nitromethane and the solution was cooled to 0°C. Fuming nitric acid (90 %, 10 ml, 215 mmol) at 0°C was added, and the reaction solution was kept at 0°C for 2 days. A small amount (ca. 10 ml) of water was added, and the new solution was extracted three times with cyclohexane. The combined cyclohexane phases were washed with water and dried with magnesium sulphate. The drying agent was removed and the solvent was evaporated. The residue was dissolved in carbon tetrachloride and analysed by means of NMR spectroscopy. The relative amounts of the two products, 1,3,5-trineopentyl-2-nitrobenzene and 2-iodo-1,3,5-trineopentyl-4-nitrobenzene, were determined by comparing the intensities of the peaks due to the different aromatic protons.

The experiment was repeated with varying amounts of sodium nitrite added to the nitric acid before the acid was added to the nitromethane solution. The results are summarized in Table 1.

When more than approximately 300 mg of sodium nitrite was added to the acid, a precipitate appeared when the acid was poured into the nitromethane solution. This precipitate was analysed by conventional chemical tests and was found to consist of sodium nitrate.

Estimate of the rate of reaction of ITNB with nitric acid with and without sodium nitrite. ITNB (20.0 mg, 0.048 mmol) was dissolved in 10.0 ml of nitromethane and the solution was cooled to 0°C. Fuming nitric acid (90 %, 2.0 ml, 43 mmol) at 0°C was added. The reaction mixture was kept at 0°C, and aliquots were withdrawn at proper time intervals. The aliquots were added to some water and the resulting solution was extracted with cyclohexane. The cyclohexane solution was analysed by means of GLC, and the relative amounts of the starting material and the two products were obtained as the

ratios of the peak heights. The value of the pseudo first-order rate constant for the consumption of ITNB was 2.1×10^{-4} s^{-1}.

The experiment was repeated with 64.6 mg (0.94 mmol) of sodium nitrite dissolved in the nitric acid before the addition to the nitromethane solution. In this case the value of the rate constant was 9.0×10^{-5} s^{-1}. The accuracy of these rate constants can be estimated at ± 10 %. Both experiments were repeated, and the values of the rate constants were found to be within the given error limits.

The relative amounts of the two products, NO_2TNB and INO_2TNB, determined by means of GLC as just described, were found to be constant throughout the reactions.

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