

## Short Communications

### Some Medium Effects on the Nitration of 2-Iodo-1,3,5-trineopentylbenzene and 2-Iodo-1,3,5-triisopropylbenzene

INGEGÄRD JOHANSSON

Department of Organic Chemistry, University of Göteborg and Chalmers University of Technology, S-412 96 Göteborg, Sweden

In the nitration of 2-iodo-1,3,5-trialkylbenzenes two main products are formed, 2-nitro-1,3,5-trialkylbenzene and 2-iodo-4-nitro-1,3,5-trialkylbenzene from nitrodeiodination and nitrodeprotonation, respectively.<sup>1–4</sup> The rate-constant ratios for these two reactions of a series of 2-iodo-1,3,5-trialkylbenzenes in a nitric acid-nitromethane medium have been reported previously.<sup>4</sup> For sterically crowded substrates, branching in the  $\alpha$ -position favours deiodination, while  $\beta$ -branching favours deprotonation. A rather large difference is found *e.g.* between 2-iodo-1,3,5-triisopropylbenzene, *1*, and 2-iodo-1,3,5-trineopentylbenzene, *2*, with deiodination – deprotonation rate ratios of 3.75 and 0.57, respectively. An explanation of the last-mentioned low ratio was sought in the interactions between the neopentyl substituents in 1,3,5-trineopentylbenzene derivatives found by Carter *et al.*<sup>5</sup> to give rise to two types of rotamer, A and B (see Fig. 1). Assuming preferential attack of the nitronium ion on the unsheltered side of rotamer A, expulsion of the iodonium ion would be hindered by the interacting alkyl branches (provided that

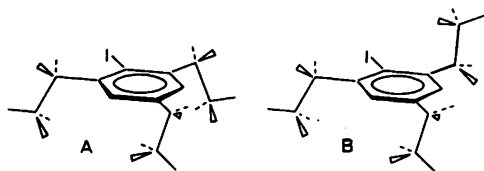


Fig. 1. Two possible rotamers of 2-iodo-1,3,5-trineopentylbenzene.

such interaction in the transition state is similar to that occurring in the ground state). Thus, the nitrodeprotonation reaction would be favoured despite the resulting increase of steric strain in the product. The present communication reports an attempt to shed some light on this problem.

In order to vary the extent of intramolecular interaction and find out the effect on the deiodination – deprotonation ratio, two methods were used – changing the solvent and changing the temperature. Both substrates *1* and *2* were investigated to see if the solvent effects are fundamentally different for these two rather different molecules.

*Results and discussion.* Four nitroalkanes, nitromethane, *a*, nitroethane, *b*, 1-nitropropane, *c*, and 2-nitropropane, *d*, were examined as solvents with the idea that the alkyl branches of these molecules would interact with the neopentyl branches of substrate *2* and thus change the intramolecular interaction possibilities. The reactions were run in organic solvent – nitric acid media with the same acid concentration and similar substrate concentrations. The kinetics show a similar pattern for all the nitroalkanes, *i.e.*, changing from zeroth to first order during the course of the reaction. Initial rates and initial nitrodeiodination – nitrodeprotonation product ratios (=rate constant ratios<sup>3</sup>) are given in Table 1. The nitrodeiodination reaction is sometimes followed by an iodination process (only with *1* in this examination) which complicates the kinetics. This secondary reaction has been examined thoroughly in previous investigations.<sup>3,4</sup> Here, only the initial product ratios are given and hence the iodination is of no significance. The kinetics of the nitration will be discussed below. As can be seen, the product ratios for *1* are the same within the error limits (*cf.*  $3.75 \pm 0.11$  as reported earlier<sup>4</sup>). The differences found with substrate *2* are also very small but a vague trend might be seen in the direction that the ratio is smaller when the solvent nitroalkane has a longer alkyl chain. This could be interpreted in terms of the above-mentioned interaction with the neopentyl branches (in this case causing a further decrease of the deiodination).

Next, one aromatic solvent, *p*-fluoronitrobenzene, *e*, was chosen to show the effect of a possible  $\pi$ – $\pi$  interaction between the solvent and the solute.

Table 1. Nitrodeiodination – nitrodeprotonation product ratios (adjusted for the number of available positions) and initial rates for the nitrations of 2-iodo-1,3,5-triisopropylbenzene, 1, and 2-iodo-1,3,5-triisopentylbenzene, 2, in the solvents *a–f*. Conditions: 4.94 M nitric acid, 1.32 M water in solvents *a–e*, respectively, at 0 °C. In solvent *f* the same amounts of acid and water were added leading to a heterogenous reaction.

Substrate	Concentration of substrate (M)	Solvent	Nitrodeiodination – nitrodeprotonation product ratio	$\frac{d[\text{ArHI}]}{dt}$ ( $10^{-6} \text{ M s}^{-1}$ )	Reaction order in the aromatic substrate
1	0.00463	<i>a</i>	3.8	0.21	0–1
1	0.00468	<i>b</i>	3.6	0.12	0–1
1	0.00466	<i>c</i>	3.7	0.18	0–1
1	0.00465	<i>d</i>	3.7	0.11	0–1
1	0.00487	<i>e</i>	3.3	1.7	1
1	0.00594	<i>f</i>	4.3		
2	0.00221	<i>a</i>	0.57	0.50	0–1
2	0.00250	<i>b</i>	0.56	0.17	0–1
2	0.00268	<i>c</i>	0.50	0.22	0–1
2	0.00321	<i>d</i>	0.52	0.18	0–1
2	0.00274	<i>e</i>	0.50	2.9	1
2	0.00263	<i>f</i>	0.64		

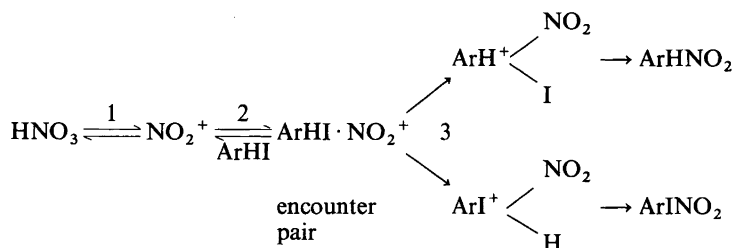
Using hexafluorobenzene as solvent, Carter *et al.*<sup>5</sup> found a different rotamer population ratio in 2,4-dibromo-1,3,5-triisopentyl-6-nitrobenzene as a consequence of the  $\pi-\pi$  interaction. The nitrodeiodination – nitrodeprotonation ratio measured in solvent *e* with the same acid concentration and in the same way as above is found to be somewhat smaller for both substrates 1 and 2 (product ratio in *e* relative to that in *a* is 0.85 for 1 and 0.875 for 2), showing no fundamental difference in this case. The product ratios and the initial rates are accounted for in Table 1. Inspection of CPK models of the Wheland intermediates for nitrodeiodination and nitrodeprotonation reveals that that of the first-mentioned reaction is the most sterically demanding one. This would mean that if a certain solvent interacts more closely (*e.g.* by  $\pi-\pi$  interaction) with the solute, the nitrodeiodination would be more hindered than the nitrodeprotonation. The increased hindrance as depicted by the models is especially obvious with substrate 2, in which a rotation of an adjacent alkyl substituent seems necessary during the rehybridization process.

A complementary study was made with carbon tetrachloride, *f*, representing a system with less interaction with the solute. The same acid concentration was used, which resulted in a heterogenous mixture. Aliquots were nevertheless taken from the reaction mixture to make sure that the product ratio was the same during the reaction. Under these conditions the deiodination – deprotonation ratio is only somewhat larger for

both substrates (product ratio in *f* relative to that in *a* is 1.13 for both, see Table 1). This may show that *f*, because it interacts very slightly with the solute, hinders the expulsion of the iodonium ion to a somewhat less extent than the other solvents do.

Investigations were also made in nitromethane with substrate 2 at two different temperatures; –28 °C (6 M acid) and 40 °C (2 M acid) to see if the different populations of the energy levels caused by the temperature increase would affect the deiodination – deprotonation ratio. This ratio was found to be 0.55 and 0.59, respectively, which, within the error limits, corresponds to what can be expected from the temperature difference according to transition state theory, assuming that there is no difference in entropy of activation between the two reactions.

**Conclusion.** The fact that the product ratio varies very little with the solvent indicates that the interaction between the solvent and the product-determining transition states is weak or, maybe more probable, that the interactions with the different solvents affect the nitrodeiodination and nitrodeprotonation reactions in the same way. The latter suggestion would mean that the product-determining transition states are rather similar. This is not self-evident in view of the differences in the electronegativity and polarizability of the two leaving substituents in question. However, as the reactions are very fast, the product-determining transition states may occur relatively early on the reaction path and thus resemble the preceding



Scheme 1.

encounter pair and not differ too much among themselves.

**Kinetics.** The most widely accepted mechanism for the nitration reaction is described in Scheme 1. The kinetics are of zeroth order in the aromatic substrate when step 1 is rate-determining and first order when 2 or 3 is rate-determining.<sup>6</sup> In this investigation, the reaction order is found to be close to first order in solvent *e* and to change from zeroth to first order during the reaction in solvents *a*–*d*.

Inspection of the initial rates given in Table 1 reveals that in *p*-fluoronitrobenzene, *e*, the nitration is faster than in nitromethane, *a*, and that *a* is the "best" solvent for nitration compared to the other nitroalkanes, *b*, *c* and *d*. The relative order of *b* and *c* is also somewhat unexpected. When the reactions are close to zeroth order in the aromatic substrates, the initial rates are a measure of the rate of the nitronium ion production (step 1 in Scheme 1). The initial rate values should thus depend on the polarity of the solvent. Physical constants change in a monotonous way when the alkane chain is elongated<sup>7</sup> and thus the initial rate should change in the same way. However, as has been pointed out by Reichardt,<sup>8</sup> "no single macroscopic physical parameter could possibly account for the multitude of solute–solvent interactions on the molecular–microscopic level".

**Experimental.** The substrates have been synthesized for earlier investigations.<sup>3,4</sup> The equipment and methods used have been described.<sup>3,4</sup> The solvents used were commercial. Purity was tested by GLC and NMR and found to be: nitromethane (Aldrich Chem. Company, spectrophotometric grade) 95% with 2% nitroethane and 3% 2-nitropropane; nitroethane (Fluka) 97% with 2.5% 2-nitropropane and 0.5% nitromethane; 1-nitropropane (Fluka) 96% with 4% 2-nitropropane; 2-nitropropane (Fluka) 98% with 2% 1-nitropropane; *p*-fluoronitrobenzene (Fluka) 99.5%. All the measurements have been made at 0 °C unless otherwise stated. As the melting point of *e* is 21 °C the substrate solution was kept at room temperature and added to the acid solution at

0 °C. The reaction mixture was then cooled down to 0 °C before the measurements started, which meant that an extrapolation to the starting point had to be made.

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