Nitration of 1,3,5-Trichloro-2,4-dinitrobenzene: Nitro-denitration

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The title reaction effected in oleum at 150 °C gives a quantitative yield based on chlorine of a mixture of 1,3,5-trichloro-2,4,6-trinitrobenzene and 1,2,3,5-tetrachloro-4,6-dinitrobenzene; the dependence of product ratios on acidity, effects of additives, and results of isotopic-labelling studies indicate that the latter product is formed *via* reversible *ipso*-attack of nitronium ion at a nitro-substituted position followed by nucleophilic capture to give a diene which gives, possibly after oxidation, chlorine in an electrophilic form for reaction with starting material.

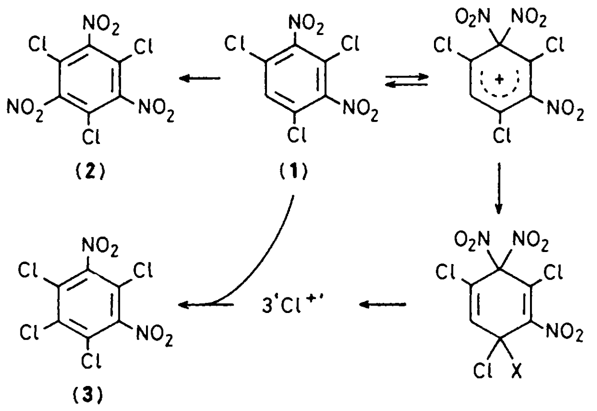
Nitration of (**1**) in oleum at 150 °C follows a rate law which is first-order in the concentration of nitric acid and of (**1**). It gives a mixture of (**2**) and (**3**). The initial ratio of yields (**2**):(**3**) increases from 50:50 in 98% H_2SO_4 to 90:10 in oleum containing a 29% excess of SO_3 by weight (29% oleum). The products, particularly (**3**), are unstable at the lower acidities but in > 11% oleum their stabilities are sufficient to establish that the overall yield based on chlorine in the starting materials and products is quantitative within experimental error.

These and the following observations cast light on the mechanism by which the unexpected product (**3**) is formed.

(i) Addition of (**2**) at the start of the reaction has no effect on the kinetics or products of reaction of (**1**). This excludes (**2**) as either the donor or recipient of the transferred chlorine; the latter must come from (**1**) and react with (**1**).

(ii) Addition of *m*-dinitrobenzene markedly diminishes the relative yield of (**3**), and chlorodinitrobenzenes can be detected amongst the products. This indicates that there is formed from (**1**) an electrophilic chlorinating agent. Since there is a 'chlorine balance' at the end of the reaction, each molecule of (**1**) which decomposes must give up all of its chlorine in this way.

(iii) If nitration of (**1**) is effected with $H^{15}NO_3$, both (**3**) and



Scheme 1

remaining (**1**), extracted after *ca.* 2 half-lives for nitration, are found to contain ^{15}N. Enrichments of (**1**) were 0.8% (2.8% oleum), 4.8% (18.7% oleum), and 5.8% (28.0% oleum).

On the basis of all this information we advance the incomplete mechanism shown in Scheme 1. Compound (**1**) reacts with NO_2^+, either at the unsubstituted position to give (**2**) or *ipso* to the nitro-group to give, reversibly, an *ipso*-Wheland intermediate. This can be captured by an unidentified nucleophilic species X (perhaps HSO_4^-) to give a diene. The partitioning of the Wheland intermediate, between return to starting material and nucleophilic capture, moves in favour of the latter as acidity decreases, thus decreasing the extent of ^{15}N-incorporation and increasing the relative yield of (**3**).

The way in which the diene decomposes is unclear, but it is suggested that under the vigorous conditions decomposition is complete and yields, perhaps after oxidation by nitric acid, 3 moles per mole of an electrophilic chlorinating agent which we loosely identify as 'Cl$^+$' in Scheme 1. These then react with (**1**) to form (**3**).

The experiments with $H^{15}NO_3$ provide the first identification of *ipso*-attack at a C–NO_2 position, and of the process of nitro-denitration.

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