Iodine Oxidation of Unsaturated Bunte Salts[1]

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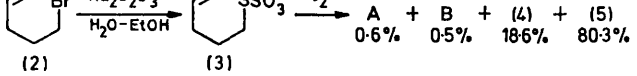
Summary Oxidation of pent-4-enyl thiosulphate with iodine in refluxing water–ethanol yielded 2-ethoxymethyltetrahydrothiophen and 2-hydroxymethyltetrahydrothiophen instead of the expected pentenyl disulphide; treatment of pentenyl disulphide with iodine in refluxing water–ethanol produced the same products and the same percent yields as the oxidation of the 4-pentenyl-1-thiosulphate.

In an attempt to prepare pentenyl disulphide (**1**), the appropriate Bunte salt, pent-4-enyl thiosulphate (**3**) was oxidized with iodine in refluxing water–ethanol.[2] However, little or no disulphide was formed. Four products were formed, the two major ones being identified as 2-hydroxymethyltetrahydrothiophen (**4**) and 2-ethoxymethyltetrahydrothiophen (**5**). The reaction sequence and products obtained, in order of increasing g.c. retention times, are shown in Scheme 1.† When the solvent system was changed from ethanol–water to methanol–water, the



Scheme 1

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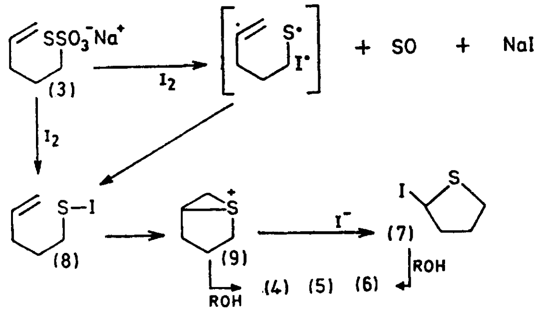
† The yields given are relative yields. The absolute yield of (**5**) was 53% and that of (**4**) was 12%.

major product was 2-methoxymethyltetrahydrothiophen (**6**), instead of (**5**).

To examine the possibility that (**1**) was an intermediate in the Bunte salt reaction, (**1**) was prepared by the reaction of (**2**) with sodium sulphide and sulphur,[3] and was subjected to the same reaction conditions employed in the Bunte salt oxidation. Four products were obtained and were identical to those formed in the iodine oxidation of (**3**) and in approximately the same yields.



Scheme 2

To test for the possibility of radical intermediates, the reaction of (**3**) with iodine was rerun in the presence of phenol, an effective radical trap.[4] Analysis of the reaction mixture showed the same four products were formed as in the absence of phenol, plus unchanged phenol. The absence of any new products suggests that no uncaged or 'free' radicals were formed in this reaction. Further, the relative yields of the products were essentially the same as when the reaction was run in the absence of phenol.

The pathway considered most likely for the iodine oxidation of (**3**) is shown in Scheme 2. In this scheme, (**3**) reacts with iodine or radical combination occurs to give the sulphenyl iodide (**8**)[5] shown. The next step is intramolecular addition of (**8**) to give an episulphonium ion (**9**)[6] which is converted into products *via* (**7**) or by attack of solvent on (**9**).

Although (**1**) reacted with iodine to give the same products as in the reaction of iodine and (**3**), it seems unlikely that the disulphide is an intermediate in this reaction. This would appear to require free or non-caged thiyl radicals which would be inconsistent with the products. It is proposed that the reaction of (**1**) with iodine proceeds‡ first to give two molecules of the sulphenyl iodide (**8**) and then the reaction proceeds as shown in Scheme 2.

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‡ The cleavage of disulphides with halogen is well known with the stability of the resulting sulphenyl halides decreasing in the order Cl > Br > I.

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