

stage. These experiments rule out the suggestion of earlier workers⁴ that the excess liberation of iodine observed in the presence of air may be due to the reduction of the penta-valent vanadium being carried beyond the tetravalent stage. We have carried out experiments to see if this excess liberation of iodine in the presence of air is due to (a) the simple autoxidation of hydriodic acid by atmospheric oxygen catalysed by tetravalent vanadium or (b) the oxidation of hydriodic acid by atmospheric oxygen induced by the primary reaction between vanadic acid and hydriodic acid. We found that at the hydrogen-ion concentration employed in the experiments the liberation of iodine due to cause (a) is negligible and cannot account for the enormous liberation of iodine actually observed. The excess liberation of iodine observed in the presence of air is, therefore, due to the induced oxidation of hydriodic acid. We also found that the induction factor (F)

$$F = \frac{\text{Number of molecules of hydriodic acid oxidised by oxygen}}{\text{Number of molecules of hydriodic acid oxidised by vanadic acid}}$$

varies with concentration of vanadate and hydrogen ion. Recently we⁵ reported that oxalate ion catalyses the reaction between vanadic acid and hydriodic acid. The presence of the catalyst also influences the magnitude of the induction factor.

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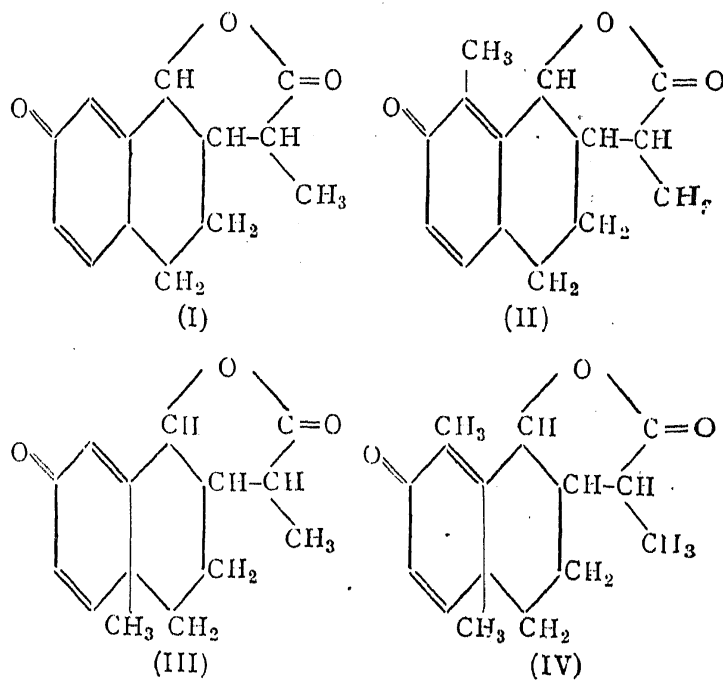
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AN ABSOLUTE ASYMMETRIC SYNTHESIS

An absolute asymmetric synthesis consists in the preparation of an optically active molecule without using at any stage of the synthesis an optically active reagent and without using any of the methods of resolution. Some cases of asymmetric synthesis using polarised light, etc., have been reported but an unequivocal synthesis without the use of such agencies has not been reported. Such an asymmetric synthesis has now been observed for the first time in our work on the synthesis of santonin and related compounds.

The synthesis of santonin (IV) has already been reported.¹ Using similar methods we have prepared compounds (I), (II) and (III).

As all these compounds were expected to be racemic an attempt was made to resolve them by the usual methods. Compounds (I) and (II) were really racemic and could be readily resolved through their strychnine salts into the dextro and lævo forms. The dextro form of (I) had $[\alpha]_D^{28} = +112$ and its lævo form



had $[\alpha]_D^{28} = -112$. Similarly the dextro form of (II) had $[\alpha]_D^{28} = +158.5$ and the lævo form had $[\alpha]_D^{28} = -158.5$.

The synthetic samples of (III) and (IV) were on the other hand optically active with $[\alpha]_D^{28} = -104$ and $[\alpha]_D^{28} = -154$ respectively. (IV) was converted into the sodium salt and fractionally precipitated as the strychnine salt by strychnine hydrochloride or strychnine. From the strychnine salt precipitated, on decomposition, it was possible to regenerate (IV) having $[\alpha]_D^{28} = -172$ (m.p. 171) identical with natural santonin. The filtrates from above gave a lævo rotatory compound having $[\alpha]_D^{28} = -108$ (m.p. 171) but no dextro rotatory isomer could be isolated. Thus an absolute asymmetric synthesis had occurred at some stage of the synthesis of these compounds. Our previous statement that synthetic santonin was racemic, therefore, requires correction. A careful study of the various stages for optical activity revealed that asymmetric synthesis must have occurred either during methylation of the formyl derivative or during its subsequent condensation with the ketone. All the rotations were determined in chloroform solution.

Further work on the mechanism of this asymmetric synthesis is in progress.

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