A Novel Bridgehead Substitution: 1-Iodoapocamphane from 1-Apocamphanol

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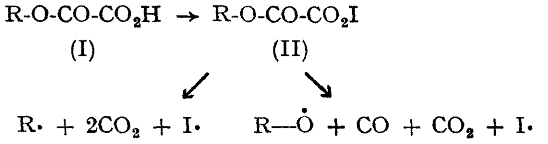
NUCLEOPHILIC SUBSTITUTIONS at bridgehead positions in bicyclic systems are energetically extremely unfavourable.[1] However numerous examples of reactions which produce bridgehead carbanions or free radicals have been demonstrated.[2] We report the substitution of a bridgehead hydroxy-group by a halogen group in a bicyclic[2,2,1]-heptane system. The decomposition of oxalate esters have been investigated[3] and alkyl radicals are produced only when the radical can stabilise by delocalisation.

Since Barton[4] has shown that irradiation of acyl hypoiodites is an effective decarboxylating reaction it was thought that this process would be a mild, but extremely effective, way of initiating the decomposition of oxalic acid half-esters (I). The acyl hypoiodite (II) could decompose either to an alkoxyl radical, carbon dioxide, and carbon monoxide or to an alkyl radical and carbon dioxide. This fragmentation would depend on the stability of the respective products.



$$\begin{tikzcd} & \underset{\text{(I)}}{\text{R-O-CO-CO}_2\text{H}} \arrow[r] & \underset{\text{(II)}}{\text{R-O-CO-CO}_2\text{I}} \arrow[dl] \arrow[dr] & \\ \text{R}\cdot + 2\text{CO}_2 + \text{I}\cdot & & & \text{R—}\dot{\text{O}} + \text{CO} + \text{CO}_2 + \text{I}\cdot \end{tikzcd}$$

To test this hypothesis, 1-apocamphanol[5] was refluxed with an excess of oxalyl chloride in ether. The acid chloride in ether was washed until hydrolysis to the acid was complete. 1-Apocamphanyl hydrogen oxalate was treated with mercuric oxide and iodine in carbon tetrachloride and irradiated, under nitrogen, with a 200 w tungsten lamp through a Pyrex water-bath kept at room temperature. The reaction gave 1-iodoapocamphane (30%) identical with a specimen prepared from apocamphane-1-carboxylic acid.[4]

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