A New Rearrangement of 1-(2-Oxocyclohepta-3,5,7-trienyl)-1-azabicyclo[2,2,2]-octanium Iodide into *m*-Hydroxybenzaldehyde

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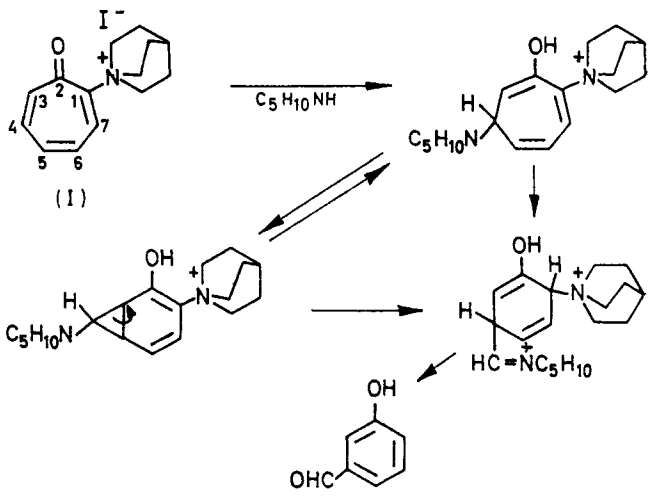
Summary The title compound (I) is converted into *m*-hydroxybenzaldehyde by piperidine in water, whereas in alkali, benzoic acid and salicylaldehyde are obtained.

MOST troponoids carrying a ring substituent with good anionic (or neutral) stability undergo ring contraction to benzenoid systems in the presence of strong bases.[1] Thus, in the presence of OH^-, benzoic acid and salicylaldehyde were obtained.[2] In a few cases, *m*-hydroxybenzaldehydes were obtained upon hydroxy-ion attack to other ring positions. This was observed only for nitro-substituted troponoids and often also required oxidising agents.[3]

We report here a new rearrangement of a troponoid into *m*-hydroxybenzaldehyde. Compound (I)[4] (0·002M) reacts rapidly in an aqueous solution of piperidine (0·02M) and piperidine hydrochloride (0·01M) at room temperature to give *m*-hydroxybenzaldehyde (70%) and 2-piperidinotropone[5] (10%). The relative yield of the substitution product, 2-piperidinotropone, is increased, slightly in the absence of hydrochloride, or markedly at high (*ca.* 1M) piperidine concentration, with or without the addition of hydrochloride. Neither benzoic acid, its piperidinamide, nor salicylaldehyde were obtained in any case.

A solution of (I) (0·002M) in aqueous sodium hydroxide (0·001M) (starting pH similar to that in the experiment with piperidine) at room temperature reacts completely within 10 min, only benzoic acid being obtained. With 0·1M-sodium hydroxide, benzoic acid and salicylaldehyde (10%) were obtained.

These results clearly show that (a) the rearrangement of (I) into *m*-hydroxybenzaldehyde is initiated by piperidine and not by hydroxy-ion attack on the troponoid (this is the first observation that a base-initiated rearrangement of a troponoid into a benzenoid system takes a different course according to the nature of the attacking base), and (b) that rearrangements into *m*-hydroxybenzaldehydes are not confined to substrates carrying nitro-groups, a quaternary nitrogen being sufficient to activate the appropriate ring position for attack by the nucleophile.



SCHEME

A plausible mechanism is outlined in the Scheme. (*E.g.* attack at ring position 4). Attacks at any one of the positions 5—7 are also suited for formation of *m*-hydroxybenzaldehyde. Rapid hydrolysis of immonium salts as in the Scheme is well documented.[6] When the reaction is followed by u.v. it is seen that at high piperidine concentration (I) disappears quite rapidly, an intermediate spectrum being generated which then changes relatively slowly into that for *m*-hydroxybenzaldehyde. Further studies are being carried out on the mechanism of this rearrangement.

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