

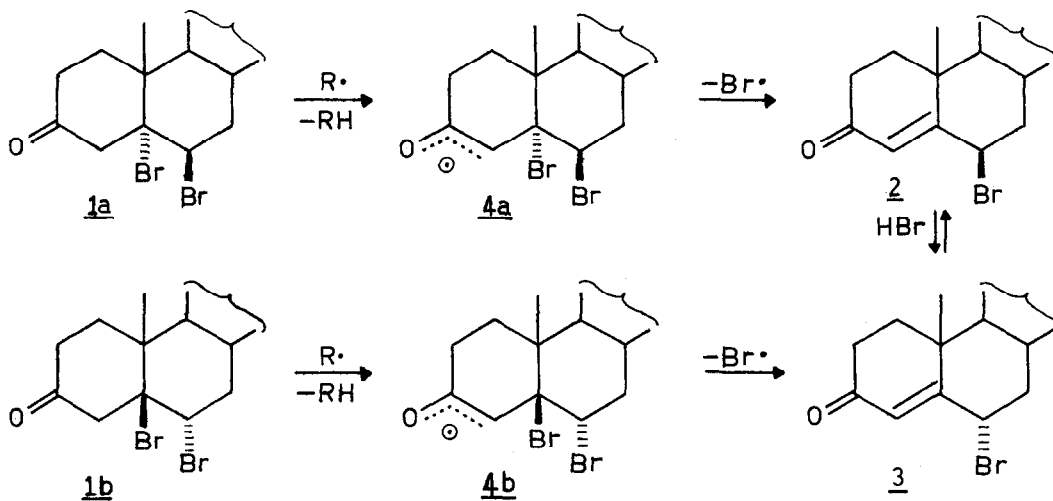
HOMOLYTIC 1,2-ELIMINATION OF HYDROGEN BROMIDE

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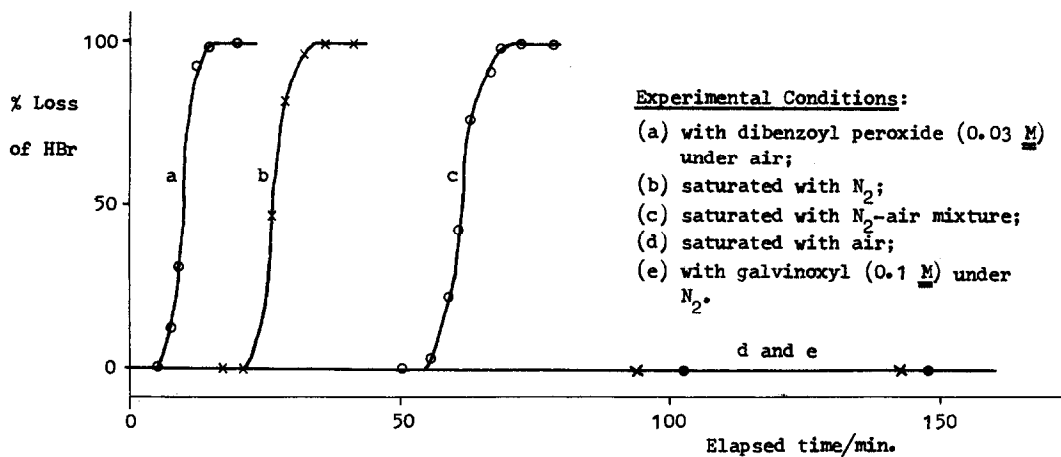
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Recently, it has been noted<sup>1</sup> that some autocatalysed brominations involving the formation of HBr may involve free-radical processes. The fact that adducts are formed accompanying the rather complex course of bromination of cholest-5-en-3-one has led us to investigate the course of elimination from 5 $\alpha$ ,6 $\beta$ -dibromocholestan-3-one (partial formula 1a) and 5 $\beta$ ,6 $\alpha$ -dibromocholestan-3-one (partial formula 1b).



The reactions can be followed by <sup>1</sup>H n.m.r. spectroscopy in deuteriochloroform as solvent, and in both cases give as products the equilibrium mixture of the two 6-bromocholest-4-en-3-ones (2 and 3).

The 5 $\alpha$ ,6 $\beta$ -dibromide (1a) reacts with an induction period which is markedly affected by the presence of such compounds as dibenzoyl peroxide, oxygen, or galvinoxyl (see figure).



**Figure:** 5 $\alpha$ ,6 $\beta$ -Dibromocholestan-3-one (0.25 M) in CDCl<sub>3</sub> at 37°C.

When treated under similar conditions, the 5 $\beta$ ,6 $\alpha$ -dibromide (**1b**) is much more reactive than **1a**, and even under oxygen decomposes in less than 1 minute. In the presence of galvinoxyl (0.02 M) under nitrogen, however, there was no detectable reaction after 2 hrs.

We suggest, therefore, that the reactions involve the intermediate radicals **4a** or **4b**, stabilised by resonance and participating in chain processes in which the propagation involves **1a** or **1b**, **4a** or **4b**, and a bromine atom, the length of each chain being greatly shortened or eliminated by the presence of scavengers, such as oxygen or galvinoxyl, which probably react preferentially either with bromine atoms or with the radical initiator.

Although the free-radical addition of HBr has been studied extensively,<sup>2</sup> there seem to have been comparatively few studies of its reversal, which in the present examples can be observed because it is favoured thermodynamically by internal strain in the starting materials and by the thermal stability of the products. The possible dual function of oxygen as a chain-initiator and as a radical-scavenger has been frequently noted.<sup>3</sup>

The final reversible isomerization of the 6-bromocholest-4-en-3-ones probably involves the usual acid-catalysed mechanism,<sup>4</sup> though free-radical isomerizations of bromides are known also.<sup>3</sup>

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#### References

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