

SULPHUR PARTICIPATION IN ELIMINATION REACTIONS

OF 9-THIABICYCLO[3.3.1]NONANES

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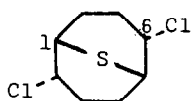
(Received in UK 7 June 1973; accepted for publication 28 June 1973)

It has been suggested^{1,2} that substitution reactions at C-2 and C-6 of the 9-thiabicyclo[3.3.1]nonane nucleus (e.g. I) are anchimerically assisted by participation of the sulphur lone pairs. We have found that the sulphur atom of this ring system may also participate in elimination reactions and report here the first cases in which 9-thiabicyclo[3.3.1]nonanes react with exclusive formation of a 9-thiabicyclo[4.2.1]nonane product.

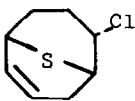
Solvolytic Elimination of Dichloride (I) and Chloroalkene (II). Reaction of I with refluxing collidine for 14 hr. gave a liquid diene, C₈H₁₀S, to which we have assigned structure III on the following evidence. The diene is conjugated as shown by the UV spectrum, by the complex four-spin vinyl absorption in the NMR spectrum and by the formation of a 1:1 adduct with 4-phenyl-1,2,4-triazoline-3,5-dione. NMR experiments are in accord with structure III (but not with IV) and the diene yields 9-thiabicyclo[4.2.1]nonane¹ on hydrogenation.

Dehydrochlorinations of I for shorter periods gave mixtures of III and chloroalkene (II), the latter assignment being confirmed by double irradiation and by direct comparison with an authentic sample.¹ Treatment of II with collidine gave III as the sole product.

Thus the solvolytic elimination of I proceeds via II by monodehydrochlorination which we suggest is followed by sulphur assisted² expulsion of chloride and elimination of an allylic proton from V. That the sulphur atom does assist dehydrochlorination is evinced by the inertness to reaction with collidine shown by the sulfoxide and sulphone analogues of I.



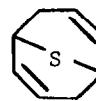
I



II



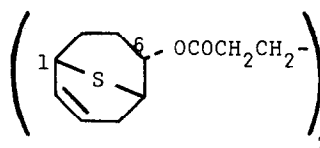
III



IV



V



VI

Pyrolytic Elimination of Adipate (VI). Pyrolysis of (VI) has been reported³ to yield diene(IV). In our hands the product of this reaction is identical to that from the collidine treatment of I and is thus the [4.2.1] isomer (III). We have found that the spectroscopic properties of VI are consistent with the assignment of a bicyclo[3.3.1] ring system;^{1,4} consequently, skeletal rearrangement must occur during elimination. However, the course of the elimination step is undefined; while a normal cis-elimination to give IV could be followed by thermal rearrangement, molecular models show that the carbonyl oxygen of the C-6 equatorial (by NMR) ester group of VI can closely approach the quasi-equatorial (C-4) hydrogen. This, together with the approximately antiperiplanar alignment of the S-C-5 and O-C-6 bonds, permits the abstraction of an allylic (C-4) hydrogen and concomitant C-5 to C-6 migration of the S-C-5 bond.

Acknowledgement. C.M.L. acknowledges the award of an S.R.C. Studentship.

References.

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- ⁴ H.J. Franz, W. Höbold, R. Höhn, G. Müller-Hagen, R. Müller, W. Pritzkow and H. Schmidt, J. Prakt. Chem., **312**, 622 (1970).