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# THE QUESTION OF A T.M.M. INTERMEDIATE (1) IN THE FLASH VACUUM PYROLYSIS OF 3-ISOPROPYLIDENE-2,2,4,4-TETRAMETHYLTHIETAN 1,1-DIOXIDE (2) AND OF 4-ISOPROPYLIDENE-3,3,5,5-TETRAMETHYL-$\Delta^{1,2}$-PYRAZOLINE (3) AND IN THE PHOTOLYSIS OF (3)

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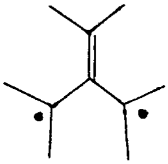

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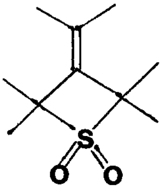

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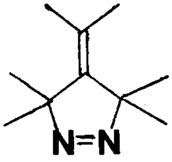

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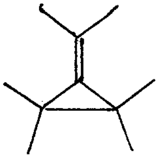

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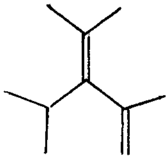

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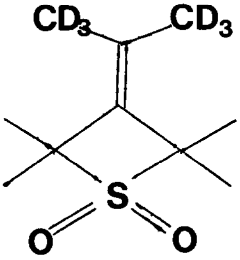
Our studies of the flash vacuum pyrolysis (F.V.P.) of the thietan dioxide 2 at 770 °C had shown that the diene 5 was produced.[1] Whilst this could be explained in terms of a T.M.M. intermediate 1 other mechanisms are also possible[2] and in an attempt to clarify the situation it was decided to study the F.V.P. behaviour over a range of temperatures and compare the behaviour of the thietane 2 and the corresponding pyrazoline 3.[3,4] Both 2 and 3 were found to give mixtures of diene 5 and methylene cyclopropane 4 and figure 1 shows how the compositions of these mixtures varied with column temperature.[5]

The data can be fitted quantitatively to a sequential first order kinetic scheme in which it is assumed that 2 or 3 → 4 → 5. In confirmation of this proposal it was shown that a similar "product ratio" curve was obtained when the cyclopropane 4 was passed through the F.V.P. column (figure 2).[6] This still does not prove that a T.M.M. intermediate is involved in these reactions and in an attempt to establish this point the specifically deuteriated compounds 6 - 8 were synthesised.



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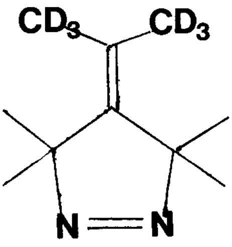

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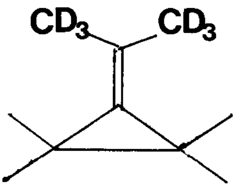

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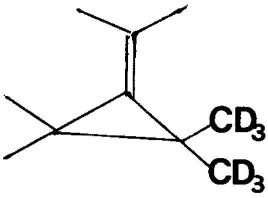

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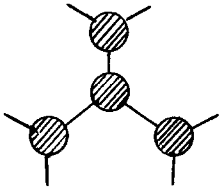
F.V.P. of the deuterated thietane 6 at the lowest practicable temperature[5] (548 °C) gave the statistical 1:2 mixture of deuterated methylene cyclopropanes 8 and 9.[7] Little can be learnt from this experiment, however, since it was shown (figure 3) that, under these conditions, 8 and 9 are rapidly interconverted. More informative were the results for the deuterated pyrazoline 7 since this could be pyrolised at temperatures below those where the interconversion of 8 and 9 is significant and it also eliminates nitrogen photochemically. It was expected that, if a T.M.M. intermediate was involved, it would adopt either a planar geometry 10 (for the triplet)or a mono-orthogonal geometry 11 (singlet) and that these would lead to product ratios 8 : 9 of 1:2 and 1:1[9] respectively. The experimental ratios for F.V.P. are shown in figure 3 from which it may be seen that there is too high a proportion of the "least motions" product to be explained in terms of either of these geometries. For example the ratio 8 : 9 obtained at 346 °C was ca. 2:1.[7]



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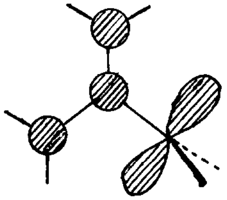

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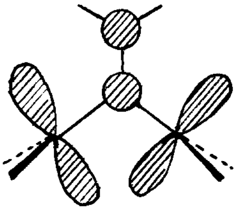

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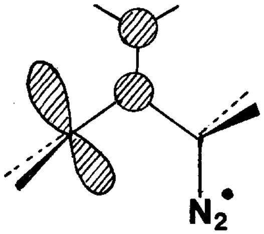

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Even more striking than the F.V.P. data is the result of photolysis. Direct photolysis of the pyrazoline 3 in benzene gives the methylene cyclopropane 4 but the deuterated pyrazoline 7 gives almost exclusively the unrearranged product 8. The results could possibly be explained in the case of F.V.P., in terms of a concerted elimination of nitrogen followed by a "hot molecule" rearrangement of the methylenecyclopropane produced but more feasible is the suggestion of a bisorthogonal T.M.M. intermediate 12 or the equivalent orthogonal diazenyl radical 13.[10] In these cases partial randomisation of the

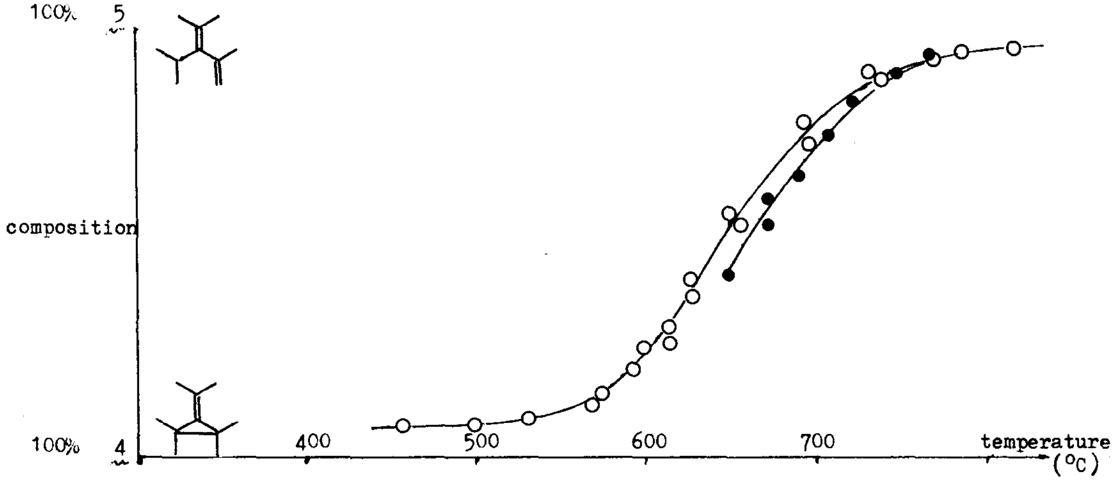

**Figure 1** Composition of the mixture of volatile products 4 and 5 obtained from F.V.P. of the thietane 2 (-●-) and the pyrazoline 3 (-o-).

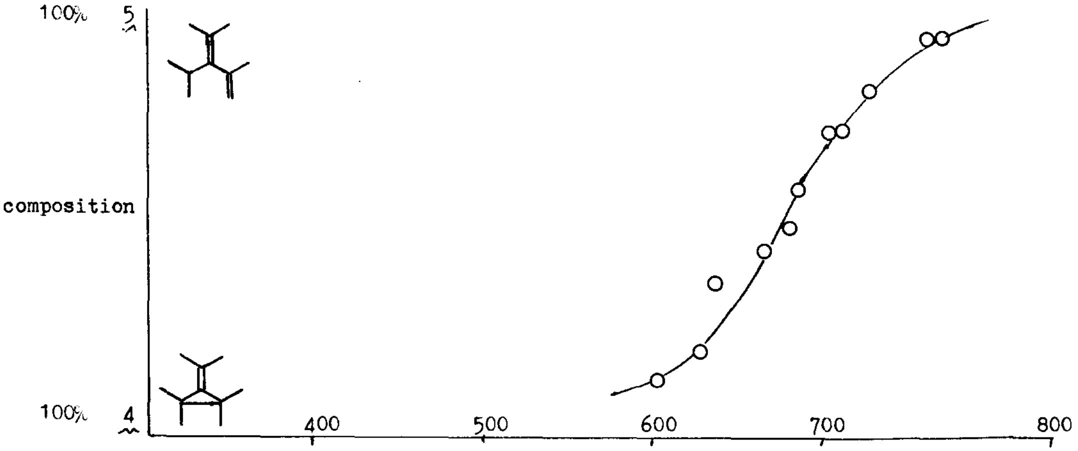

**Figure 2** Conversion of the cyclopropane 4 to the diene 5 under the same F.V.P. conditions.

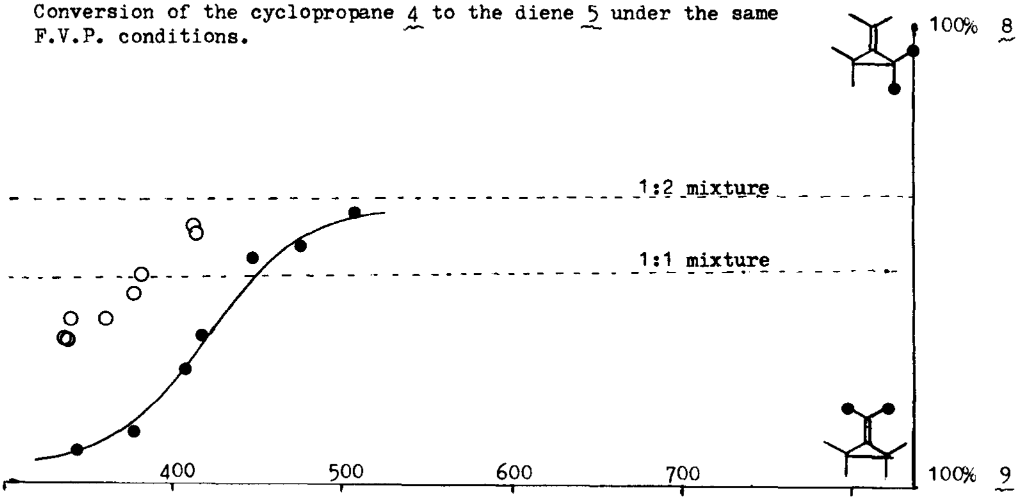

**Figure 3** F.V.P. conversion of the deuterated cyclopropane 9 to a mixture of 8 and 9 (-●-) and ratios of 8 and 9 obtained by F.V.P. of the pyrazoline 7.(o)

label could arise by competitive symmetrisation of an allyl portion before ring closure.

It is interesting to note that, in contrast to the results of pyrolysis and direct photolysis, triplet sensitised photolysis of the pyrazoline gives essentially a statistical 1:2 mixture of 8 and 9, a result which is consistent with a planar geometry 10 for the T.M.M. triplet.

## References and Notes

1 R. J. Bushby, J.C.S. Perkin I, 1975, 2513

2 Other mechanisms may be written involving, for example, an initial ring opening analogous to that found in the rearrangement of 2,2,4,4-tetramethylthietan-3-one 1-oxide. R. J. Bushby, J.C.S. Perkin I, 1976, 2590.

3 Experimental evidence exists to suggest that 4-alkylidenepyrazolines decompose thermally via a T.M.M. intermediate. R. J. Crawford and D. M. Cameron, J. Amer. Chem. Soc., 1966, 88, 2589. J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, J. Amer. Chem. Soc., 1971, 93, 1544, and subsequent papers.

4 R. J. Bushby and M. D. Pollard, Tet. Let., 1977. 3671.

5 F.V.P. experiments were performed, as described previously (ref. 1), by subliming the compound through a heated silica tube. The data for the thietane could not be extended to cover the same range as the pyrazoline as, at the lower temperatures, essentially only starting material was recovered. For similar reasons data for the pyrazoline could not be obtained below ca. 345 °C.

6 The small displacement between the curves could be the result of hot molecule rearrangement of the cyclopropane following departure of the leaving group, but the alternative explanation, that some diene arises directly from the starting material, cannot be wholly eliminated at the present time.

7 Recovered starting material showed no detectable deuterium scrambling. c.f. D. Cichra, M. S. Platz and J. A. Berson, J. Amer. Chem. Soc., 1977, 99, 8507.

8 Prepared by the method of M. S. Newman and T. B. Patrick, J. Amer. Chem. Soc., 1969, 91, 6461; but starting with $d_6$-acetone.

9 Using the least-motion route to this type of intermediate as proposed by R. J. Crawford and H. Tokunaga, Canad. J. Chem., 1974, 52, 4033.

10 R. J. Crawford, H. Tokunaga, L. M. H. C. Schrijer, J. C. Goddard, Canad. J. Chem., 1978, 56, 998.

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