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THE GENERATION AND SIGMATROPIC REARRANGEMENT OF A DERIVATIVE OF VINYL-TMM (2,5-DIMETHYL-3-ISOPROPYL-4-ISOPROPYLIDENEHEX-2-EN-1,5-DIYL)

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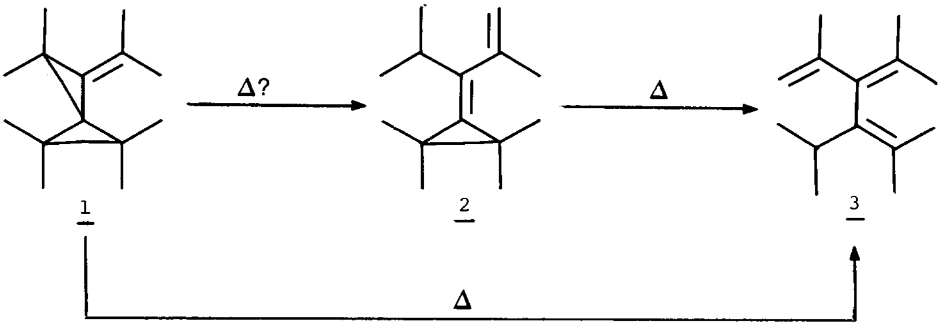
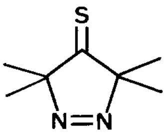
The thermal rearrangement of 2,5-dimethyl-3-isopropyl-4-isopropylidenehex-2-en-1,5-diyl to 4-isopropyl-3-isopropylidene-2,5-dimethylhexa-1,4-diene involves a 1,6-sigmatropic shift of hydrogen which may occur in an antarafacial manner.

One possible mechanism for the thermal isomerisation of methylenespiropentane 1 to triene 3[1] involves an intermediate allylidenecyclopropane 2[2]. We have now made this putative intermediate and shown that it isomerises to 3 considerably faster than does spirocompound 1; evidence for its intermediacy which is permissive but no more. Indeed the mechanism of the rearrangement of 1 to 3 and related reactions still remains in doubt[2]. We were, however, able to obtain some interesting insights into the mechanism of the allylidenecyclopropane 2 to triene 3 rearrangement.



Previous experience in the synthesis of alkylidene-2,2,3,3-tetramethylcyclopropanes[1,3] suggested that it would be possible to obtain compound 2 through the reaction of thioketone 4 and the diazoalkane 5a (or its synthetic equivalent).



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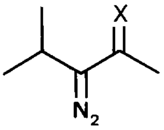
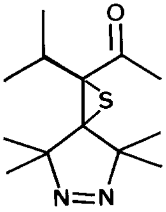


5a X = CH_2

5b X = O



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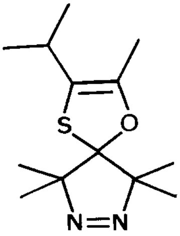

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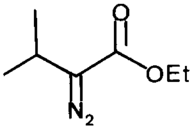
Vinyl diazoalkanes are unstable, readily cyclise and are often difficult to obtain[4]. The diazoalkane 5a proved no exception. The diazoketone 5b[5] appeared to be an obvious synthetic alternative but with thioketone 4 this gave, not the desired episulphide 6, but the 1,3-oxathiole 7[6,7]. Success was eventually achieved through the reaction of thioketone 4 with the diazoester 8[8]. This gave an episulphide which on treatment with trimethylphosphite gave the alkene 9[9]. Direct photolysis then gave 10 as the only significant product[3,10].



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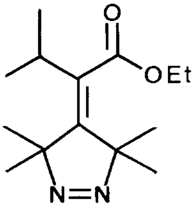

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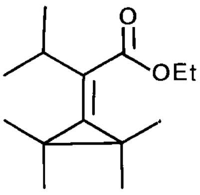

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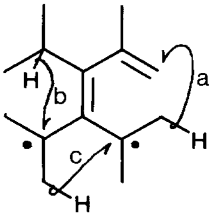

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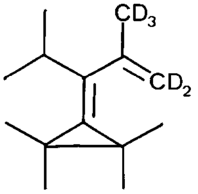
From the ester 10 the desired alkene 2 could be obtained easily by reaction with excess methyl lithium and dehydration of the resultant tertiary alcohol by heating at 70°C, under vacuum, with $KHSO_4$. The allylidenecyclopropane 2 could be converted to the triene 3 either by heating at 200°C in degassed o-dichlorobenzene (sealed tube) or by flash vacuum pyrolysis[11,12]. Considering the mechanism of this thermal rearrangement it seems reasonable to suggest that the first step involves homolysis of the 2,3-bond of the cyclopropane to give a vinyl-TMM biradical 11[13]. From this biradical there appear to be three possible routes to the triene 3. The 1,6-hydrogen shift "a" and the 1,4-hydrogen shift "b" lead directly to 3. The 1,4-hydrogen shift "c" gives initially a linearly-conjugated triene which (provided it is generated as shown in an E configuration) can rearrange to 3 via a 1,5-hydrogen shift. The distinction between these three mechanisms was easily made by deuterium labelling. The specifically deuterated derivative of 2, 12



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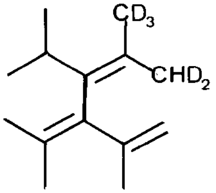

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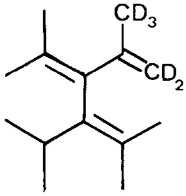

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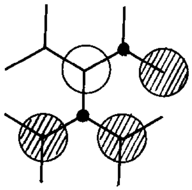

15 - (HOMO 11)

was prepared using CD_3Li in the penultimate step instead of CH_3Li. If 12 were to rearrange via "route a" the only product would be 13, "route b" would give product 14 and "route c" a roughly equal mixture of 13 and 14. In practice ^1H and ^2H-nmr confirmed that FVP of 12 gave only isomer 13. If we assume that (like their cycloaddition reactions[14]) the sigmatropic rearrangements of singlet non-Kekulé polyenes can be treated as orbital symmetry controlled processes[15] then we can rationalise this result by reference to the HOMO 15[16] of the vinyl-TMM 11. From this it may be seen that the 1,4-hydrogen shift "b" could be suprafacial whereas the 1,6-hydrogen shift "a" and the 1,4-hydrogen shift "c" are both constrained to occur in an antarafacial manner. In fact the presence of the isopropyl substituent makes it difficult to attain the required near-planar geometry for the suprafacial shift "b" and of the two possible antarafacial shifts the 1,4-shift seems intrinsically unlikely leaving the observed 1,6-shift as the most readily accessible reaction pathway.

References and Notes

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12. It is interesting to compare the thermal rearrangement of **2** with that of other allylidenecyclopropanes, most of which give the product of a formal 1,5-shift of carbon (an alkylidenecyclopent-2-ene). T. C. Shields, W. E. Billups and A. R. Lepley, *J. Amer. Chem. Soc.*, 1968, **90**, 4749; A. S. Kende and E. E. Riecke, *J. Amer. Chem. Soc.*, 1972, **94**. 1397; W. R. Roth and Th. Schmidt, *Tet. Lett.*, 1971, 3639; M. F. Semmelhack and R. J. DeFranco, *J. Amer. Chem. Soc.*, 1972, **94**, 2116.
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14. J. A. Berson in "Diradicals", ed. W. T. Borden, John Wiley 1982 and references therein.
15. A similar FMO treatment also provides a possible explanation for the isomerisation of 2-isopropylidenecyclopenta-1,3-diyl to isopropenylcyclopentene (1,4-suprafacial) rather than 3-isopropylidenecyclopentene (1,4-antarafacial) (ref. 14), but in some cases does seem to require 1,4-antarafacial shifts to occur; for example in the isomerisation of 3-dicyanomethylene-2,4-dimethylpenta-2,4-diyl to 3-dicyanomethylene-2,4-dimethylpentene (ref 11b).
16. H.M.O. Calculation. Parameters from A. Streitwieser, MO Theory for Organic Chemists, John Wiley, 1961.

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