Thermal Decomposition of *r*-1,*c*-2-Dideuterio-*t*-3,*t*-4-dimethylcyclobutane

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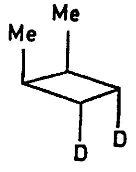
Summary Pyrolysis of the title compound which gave nearly 50:50 mixtures of *cis*- and *trans*-but-2-enes and 1,2-dideuterioethylene may proceed entirely by a biradical pathway.

It has been predicted that if the reversal of the simple [2 + 2] cycloaddition is a concerted process, the stereochemical relationships at three of the four carbons will be retained in the products.[1] Experimental verifications of this prediction [2a–c] however, have not led to any generalization concerning the mechanism of decomposition of all cyclobutanes.



(I)

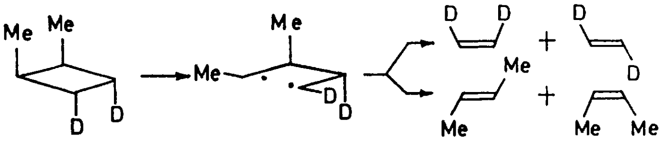
None of the experimental work that has been carried out so far has involved a simple cyclobutane with suitable labels to follow the stereochemistry at each carbon. We report the results of our study of the pyrolysis of *r*-1,*c*-2-dideuterio-*t*-3,*t*-4-dimethylcyclobutane (I).

Compound (I) was prepared by the reduction of 3,4-dimethylcyclobutene with deuteriodi-imide[2b,3] or Adam's catalyst and deuterium gas (1 atm). Both samples proved to be identical in their spectral properties [which conformed to structure (I)] and their pyrolytic behaviour.

The thermal decomposition of samples of (I) was studied in the vapour phase at 420° to 430°, 90 to 140 Torr in conditioned Pyrex cells.[4] Both the composition of the products and the half-lives of the various decomposition modes were similar to those described in *cis*-1,2-dimethylcyclobutane.[5] In particular, the *cis* to *trans* isomerization of (I) was a slow process which did not interfere with the decomposition when the conversion was kept low (< 25%).

The C_2 fraction was separated from the products by distillation at −154° and analysed by i.r. spectrometry. These spectra were compared to the spectra of synthetic mixtures of *cis*- and *trans*-1,2-dideuterioethylene until an almost exact match of the spectra was obtained.†‡ The C_4 fraction was analysed by gas chromatography.

From four runs, the average composition of the [1,2-$^2H_2$]-ethylene fraction was found to be *cis*:52 ± 3% and *trans*: 48 ± 3%. From 10 runs, the composition of the but-2-enes was found to be *cis*:56 ± 2% and *trans*:44 ± 2%.



These results suggest that the formation of but-2-ene and [1,2-$^2H_2$]ethylene from (I) proceed sequentially (Scheme). Earlier observations[5] that the *cis* stereochemistry of the methyl groups is only partially carried over to the but-2-enes are confirmed here. The rotation of the substituent groups in the biradical can be expected to favour the lighter D atom so the formation of [1,2-$^2H_2$]ethylene as a near equilibrium mixture supports the biradical hypothesis.

A conflicting point of view based on orbital symmetry may appear equally plausible. Thus, the yield of 48% of *trans*-[1,2-$^2H_2$]ethylene can be linked to a corresponding yield of *cis*-but-2-ene and 44% of the *cis*-[1,2-$^2H_2$]ethylene can be coupled to 44% of the *trans*-but-2-ene. In all, 92% of the reaction may seem to proceed by a concerted pathway.

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† Both low-resolution (Perkin-Elmer Infracord) and high-resolution (Cary 90) spectrometers were used. The latter offered no significant advantage in this particular analysis.

‡ The pyrolysate contained 10% of C_2H_3D and C_2H_4 whereas the reference materials contained no more than 1% of these compounds. Pure *cis*- and *trans*-1,2-dideuterioethylene were obtained from Merck, Sharpe and Dohme of Canada, Ltd., Montreal.

But this high degree of concertedness would be incompatible with earlier results on bicyclic cyclobutanes[2a,b] which have less rotational freedom than (I), hence this interpretation is unlikely.

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