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Thermolyses of *cis*- and *trans*-2,2,3,4-Tetramethyloxetane

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The thermolyses of *cis*- and *trans*-2,2,3,4-tetramethyloxetane were studied at temperatures between 408.0 and 477.0 °C and initial reactant pressures from 5.0 to 10.0 Torr.† Both compounds undergo parallel unimolecular reactions producing either 2-methylbut-2-ene and acetaldehyde [path (a)] or but-2-ene and acetone [path (b)].

For the *trans* isomer the following rate expressions were found:

$$\log_{10}(k_a/\mathrm{s}^{-1}) = (14.50 \pm 0.35) - (237.0 \pm 4.18\ \mathrm{kJ\ mol^{-1}})/2.303\ \boldsymbol{RT}$$
$$\log_{10}(k_b/\mathrm{s}^{-1}) = (15.00 \pm 0.40) - (261.5 \pm 5.02\ \mathrm{kJ\ mol^{-1}})/2.303\ \boldsymbol{RT}.$$

The ratio of *cis*-but-2-ene to *trans*-but-2-ene was 0.25 ± 0.02.

For the *cis* isomer the corresponding rate expressions are:

$$\log_{10}(k'_a/\mathrm{s}^{-1}) = (13.90 \pm 0.76) - (229.0 \pm 10.0\ \mathrm{kJ\ mol^{-1}})/2.303\ \boldsymbol{RT}$$
$$\log_{10}(k'_b/\mathrm{s}^{-1}) = (14.10 \pm 0.83) - (246.6 \pm 10.9\ \mathrm{kJ\ mol^{-1}})/2.303\ \boldsymbol{RT}.$$

The ratio of *cis*-but-2-ene to *trans*-but-2-ene in this case was 3.45 ± 0.30. All error limits are the 95% confidence limits.

Comparison of the Arrhenius parameters with those for other oxetane decompositions and with thermochemical estimates make it unlikely that both paths proceed *via* biradical intermediates. It is suggested that for both isomers the data are consistent with a biradical path for the production of but-2-ene but that the major path to 2-methylbut-2-ene is a concerted reaction involving a twisted activated complex.

Previous work[1] on the thermolysis of 2,2-dimethyloxetane showed that of the two parallel unimolecular reactions leading either to isobutene and formaldehyde or ethene and acetone, the former was favoured. The Arrhenius parameters for the isobutene path could not be reconciled with a biradical mechanism and it was suggested that a concerted mechanism *via* a twisted ($\sigma_{2s} + \sigma_{2a}$) activated complex would favour this path on the basis of orbital-symmetry arguments. Since this particular oxetane was the first example showing such a difference in Arrhenius parameters for the two paths, it was decided to investigate other oxetanes which are *gem* disubstituted in the 2-position.

EXPERIMENTAL

Samples of *cis*- and *trans*-2,2,3,4-tetramethyloxetane were prepared by photocycloaddition.[2] A solution of *cis*-but-2-ene (30 g) in acetone (130 g) was irradiated for 20 h in a water-cooled quartz photoreactor, using a centrally positioned 450 W medium-pressure mercury arc. The

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† 1 Torr = 133.33 Pa.

photoproduct was distilled and the fractions analysed by g.l.c. (3% silicone oil SE 30, 65 °C) to give a fraction with b.p. 110–120 °C/760 mmHg (2.2 g) rich in the two main products (ratio 2:1). These were separated by preparative g.l.c. (20 ft × 3/8 in. 7% silicone oil SE 30 on PhaseSep W at 65 °C and 20 p.s.i.).† The first-eluted compound was *trans*-2,2,3,4-tetramethyloxetane:[3] $\nu_{max.}$ (film) 2975, 1455, 1370, 1260, 1060, 955, 885 and 845 cm^{-1}; δ_H (60 MHz, CCl_4) 4.20 (dq, *J* 7 and 6.5 Hz, 1 H, H-4), 2.20 (quintet, *J* 7 Hz, 1 H, H-3), 1.29 (s, 3 H, CH_3-2), 1.27 (d, *J* 6.5 Hz, 3 H, CH_3-4), 1.22 (s, 3 H, CH_3-2) and 1.01 (d, *J* 7 Hz, 3 H, CH_3-3); δ_C ($CDCl_3$) 82.2 (C-2), 79.2 (C-4), 46.3 (C-3), 31.7 (CH_3-2), 23.3 (CH_3-4), 22.9 (CH_3-2) and 12.9 (CH_3-3). The next-eluted isomer was *cis*-2,2,3,4-tetramethyloxetane:[3] $\nu_{max.}$ (film) 2970, 1465, 1375, 1160, 1150, 1060, 1025, 960 cm^{-1}; δ_H (60 MHz, CCl_4) 4.78 (dq, *J* 8 and 6.5 Hz, 1 H, H-4), 2.64 (quintet, *J* *ca.* 8 Hz, 1 H, H-3), 1.37 (s, 3 H, CH_3-2), 1.17 (s, 3 H, CH_3-2), 1.16 (d, *J* 6.5 Hz, 1 H, CH_3-4) and 0.99 (d, *J* 7.5 Hz, 1 H, CH_3-3); δ_C ($CDCl_3$) 83.2 (C-2), 74.1 (C-4), 40.1 (C-3), 30.3 (CH_3-2), 24.8 (CH_3-2), 17.9 (CH_3-4) and 9.2 (CH_3-3).

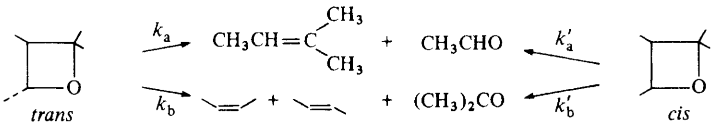
Further analysis of the purity of these samples prior to use using g.l.c. with a carbowax 20M and also a silicone oil column showed the *trans* compound to be 96.5% pure with no *cis* impurity and the *cis* compound to be 92.8% pure with 0.5% *trans* impurity. In both cases the major impurities were of lower boiling point material. Since only small samples were available (*ca.* 500 mg) it was only possible to make a small improvement in purity by on-line trap-to-trap distillation from a slush bath at −57 °C.

APPARATUS

The apparatus and procedure have been described previously.[1,4] Two Pyrex reaction vessels were used, one of volume 269 cm^3 and surface/volume ratio of 1.08 cm^{-1} and the other a packed vessel of volume 147.6 cm^3 and surface/volume ratio of 11.6 cm^{-1}. The reaction products were analysed by g.l.c. using a column composed of 1 m 10% oxydipropionitrile on Chromosorb P (960–80 mesh) and 4 m 14% bis-2-methoxyethyl adipate with 7% di-2-ethylhexyl sebacate on Chromosorb P (80–100 mesh), operated at 60 °C. Pressure changes during thermolysis were measured by an S.E.L. pressure transducer (1150D).

RESULTS

Thermolyses of *trans*- and *cis*-2,2,3,4-tetramethyloxetane gave *cis*- and *trans*-but-2-ene, 2-methylbut-2-ene, acetone and acetaldehyde as major products, in agreement with the expected unimolecular reactions, *viz*.



Support for this stoichiometry was provided by the close agreement of the measured presssure changes and the sum of the amounts of olefinic products (2-methylbut-2-ene, *cis*- and *trans*-but-2-ene).

Minor products of methane, ethane, ethene, propane, propene, but-1-ene, isobutene, 3-methylbut-1-ene, 2-methylbut-1-ene and *trans*- and *cis*-pent-2-ene were detected.

Analysis of the *cis*-2,2,3,4-tetramethyloxetane and *trans*-2,2,3,4-tetramethyloxetane remaining after thermolysis showed no interconversion of isomers to have occurred.

The decompositions appeared to follow first-order kinetics although at the low percentages of reaction normally studied (< 20%) it was not possible to exclude the existence of a higher-order component from the measured pressure traces. Rate

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† 1 ft = 30.48 × 10^{-2} m; 1 in. = 2.54 × 10^{-2} m; 1 p.s.i. = 6.895 × 10^3 Pa; 1 mmHg = 13.5951 × 980.665 × 10^{-2} Pa.

Table 1. Rate constants and product ratios for *trans*-2,2,3,4-tetramethyloxetane

temperature/°C	$k_{\text{overall}}/10^{-3}\ \text{s}^{-1}$	R^a	$k_a/10^{-3}\ \text{s}^{-1}$	$k_b/10^{-4}\ \text{s}^{-1}$
411.2	0.284	23.8	0.273	0.115
412.2	0.282	23.6	0.270	0.115
412.6	0.285	23.6	0.277	0.117
412.7	0.300	23.5	0.287	0.122
421.2	0.480	22.2	0.460	0.207
421.2	0.471	22.2	0.450	0.203
431.1	1.13	20.4	1.08	0.527
434.3	1.12	20.4	1.06	0.521
452.9	3.13	18.2	2.89	1.59
452.9	3.12	18.2	2.96	1.63
452.9	3.05	18.2	2.97	1.63
475.7	10.72	15.9	10.10	6.34
476.5	10.16	15.8	9.56	6.04
476.5	9.61	15.8	9.04	5.71

[a] $R = P$(2-methylbut-2-ene)/P(*cis*- + *trans*-but-2-ene).

Table 2. Rate constants and product ratios for *cis*-2,2,3,4-tetramethyloxetane

temperature/°C	$k'_{\text{overall}}/10^{-3}\ \text{s}^{-1}$	R^a	$k'_a/10^{-3}\ \text{s}^{-1}$	$k'_b/10^{-4}\ \text{s}^{-1}$
408.8	0.233	16.69	0.220	0.132
408.8	0.224	16.69	0.211	0.127
425.3	0.622	15.46	0.584	0.378
425.3	0.584	15.46	0.548	0.355
425.4	0.608	15.45	0.571	0.370
425.6	0.592	15.44	0.556	0.360
442.2	1.45	14.35	1.36	0.947
442.3	1.44	14.34	1.35	0.939
442.4	1.46	14.34	1.36	0.950
456.9	3.95	13.48	3.68	2.73
457.2	4.00	13.47	3.72	2.76
457.3	4.03	13.46	3.75	2.79
457.8	4.08	13.43	3.80	2.83
477.7	11.40	12.40	10.60	8.51
477.7	12.24	12.40	11.30	9.13

[a] $R = P$(2-methylbut-2-ene)/P(*cis*- + *trans*-but-2-ene).

constants derived from first-order log plots are shown as k_{overall} (*trans* compound) and k'_{overall} (*cis* compound) in tables 1 and 2. Rate constants k_a, k_b, k'_a, k'_b for the individual reaction paths (also listed in tables 1 and 2) were obtained from these using the ratio R = 2-methyl-but-2-ene/(*cis*- + *trans*-but-2-ene) measured chromatographically at various temperatures.

For the *trans* compound a series of 46 runs in the temperature range 411.2–476.5 °C and with initial pressures from 5 to 10 Torr gave

$$\log_{10}(k_a/\text{s}^{-1}) = (14.50 \pm 0.35) - (237.0 \pm 4.18\ \text{kJ mol}^{-1})/2.303\ RT$$

$$\log_{10}(k_b/\text{s}^{-1}) = (15.00 \pm 0.40) - (261.5 \pm 5.02\ \text{kJ mol}^{-1})/2.303\ RT.$$

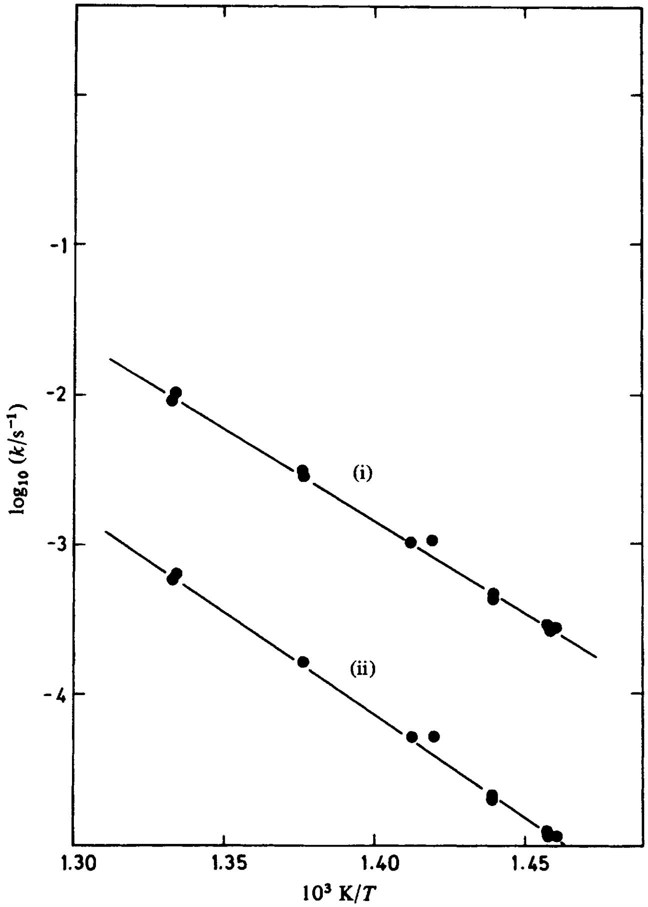


Fig. 1. Arrhenius plot for *trans* reactant for (i) path (a) and (ii) path (b).

For the *cis* compound, 41 runs in the temperature range 408.8–477.7 °C and initial pressures from 5 to 10 Torr gave

$$\log_{10}(k'_a/\mathrm{s}^{-1}) = (13.90\pm0.76)-(229.0\pm10.0\ \mathrm{kJ\ mol}^{-1})/2.303\ \boldsymbol{R}T$$

$$\log_{10}(k'_b/\mathrm{s}^{-1}) = (14.10\pm0.83)-(246.6\pm10.9\ \mathrm{kJ\ mol}^{-1})/2.303\ \boldsymbol{R}T.$$

In all cases the error limits are the 95% confidence limits. Arrhenius plots of the data for the *trans* reactant are shown in fig. 1 and for the *cis* reactant in fig. 2.

The small amount of starting material available precluded any extended test of the pressure dependence of the first-order rate constants. The larger error parameters in the rate expressions for the *cis* compound may reflect the lower purity of that compound in relation to the purity of the *trans* isomer.

Thermolyses in the packed vessel (table 3) show no heterogeneous contribution to the reactions of the *trans* compound. For the *cis* compound the increase in rate constant relative to that in the unpacked vessel shows the presence of *ca.* 3–4% heterogeneous reaction. Some runs were done in the presence of ammonia to test for

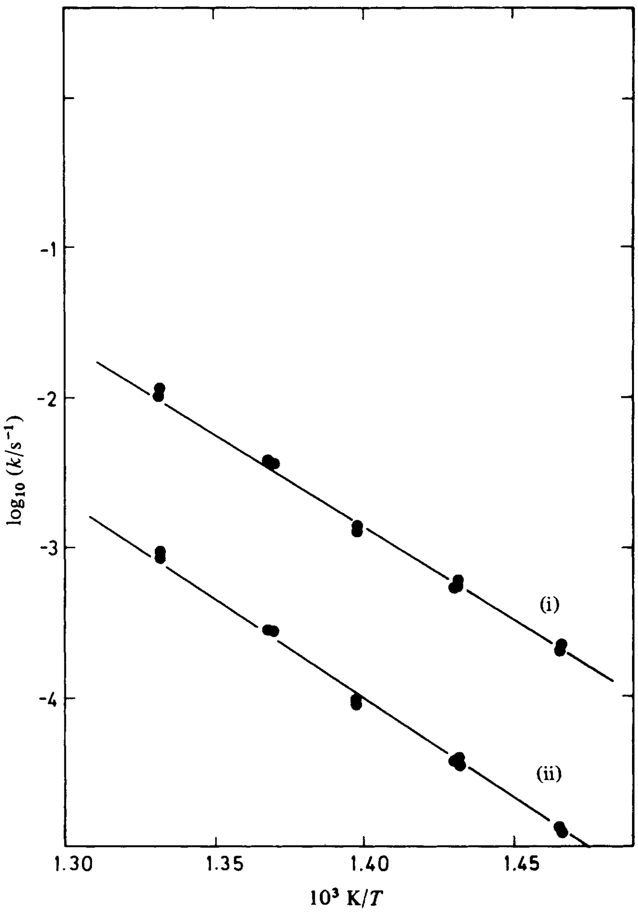


Fig. 2. Arrhenius plot for *cis* reactant for (i) path (a′) and (ii) path (b′).

possible involvement of polar intermediates but no effect on the rate constants was observed.

Additions of nitric oxide were made to test for the presence of free-radical reactions although the results of such tests are sometimes ambiguous. No effects were, however, observed on the measured rate constants (table 4).

The thermolyses by path (b) to produce but-2-ene occur with some inversion of configuration but not complete equilibration, as can be seen from fig. 3, in which the observed ratios of *cis*-but-2-ene/*trans*-but-2-ene are compared with the equilibrium values[5] at various temperatures.

DISCUSSION

The major products and observed stoichiometry confirm the overall reaction paths suggested. It is likely that the small amounts of minor products are due to the subsequent decomposition or isomerisation reactions of 2-methylbut-2-ene. Methylbutenes are known to decompose and isomerise in this temperature range.[6] Because

Table 3. Thermolyses in the packed reaction vessel ($s/v = 11.6\ \text{cm}^{-1}$)

temperature/°C	$k_{\text{overall}}/10^{-3}\ \text{s}^{-1}$	R^a	r^b	$k^c_{\text{calc}}/10^{-3}\ \text{s}^{-1}$
	trans-2,2,3,4-tetramethyloxetane			
434.2	1.06	21.2	0.20	1.07
434.5	0.99	21.8	0.20	1.08
434.5	1.07	22.1	0.21	1.08
434.7	0.97	21.1	0.21	1.10
434.5	0.97	23.3	0.21	1.08
434.7	0.99	21.7	0.22	1.10
434.4	0.99	21.4	0.20	1.08
434.5	1.09	21.8	0.21	1.08
	cis-2,2,3,4-tetramethyloxetane			
434.0	1.46	13.48	2.21	1.13
435.5	1.44	14.03	2.23	1.10
433.8	1.46	13.76	2.18	1.12
434.3	1.51	13.72	2.19	1.15
433.7	1.55	14.54	2.13	1.11
434.2	1.53	13.70	2.23	1.15
433.9	1.48	13.35	2.22	1.13
434.2	1.52	13.45	2.17	1.15

[a] R as defined in tables 1 and 2. [b] $r = P(cis\text{-but-2-ene})/P(trans\text{-but-2-ene})$. [c] Calculated from the appropriate rate expression derived from thermolyses in the unpacked vessel.

Table 4. Thermolyses in the presence of nitric oxide

temperature/°C	$k_{\text{overall}}/10^{-3}\ \text{s}^{-1}$	R^a	r^a	NO (%)
	trans-2,2,3,4-tetramethyloxetane			
437.0	1.22	18.8	0.24	18.2
436.7	1.14	18.9	0.24	21.2
436.8	1.37	19.2	0.24	28.0
436.4	1.24	18.9	0.24	22.1
437.0	1.20	19.0	0.24	22.4
	cis-2,2,3,4-tetramethyloxetane			
450.2	3.07	13.62	3.44	0.0
449.2	2.73	13.85	3.52	8.7
450.1	3.04	13.56	3.34	21.5
450.0	2.96	14.10	3.25	21.7
450.1	2.97	13.84	3.51	32.3
450.0	2.88	13.92	3.50	34.1

[a] R and r defined as in tables 1–3.

of secondary decomposition, thermolyses were limited to < 20% decomposition when the amounts of minor products were negligible.

From results in the packed vessel and from runs in the presence of nitric oxide it is probable that, as for other alkyl-substituted oxetanes, these are homogeneous unimolecular reactions.

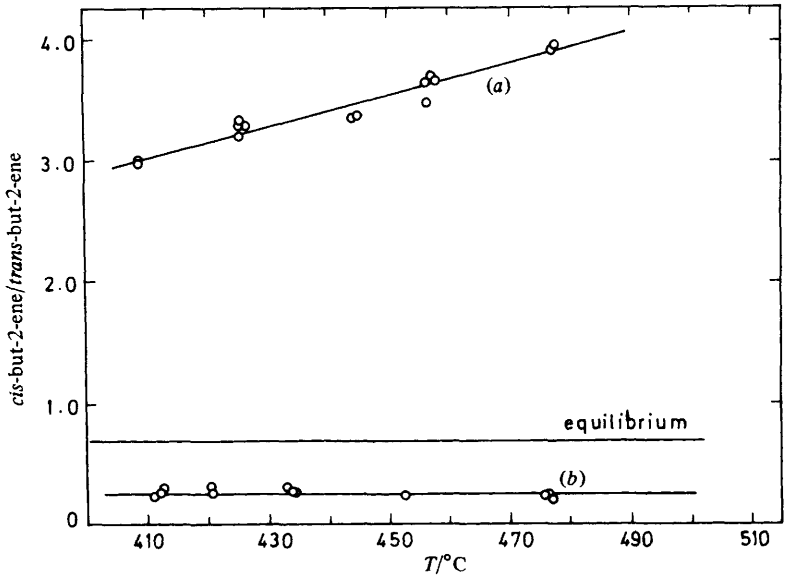
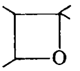


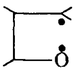
Fig. 3. Ratio *cis*-but-2-ene/*trans*-but-2-ene for (*a*) *cis* and (*b*) *trans* reactants.

Table 5. ΔH/kJ mol^{-1} (calc.) for  ——→ biradical.

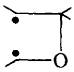
starting material	I	II	III	IV
trans	233.2	225.5	217.6	240.6
cis	232.2	224.5	216.6	239.6

The most obvious mechanism is the biradical mechanism which has been found to account adequately for many other oxetane thermolyses such as those of oxetane itself[7] and *cis*- and *trans*-2,3-dimethyloxetane.[8]

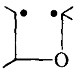
There are four possible biradical intermediates from 2,2,3,4-tetramethyloxetane, *viz*.



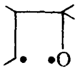
I



II



III



IV

Estimates for the enthalpy of formation of each of these biradicals from either the *trans* or the *cis* starting material can be made according to Benson's rules.[9] The results are given in table 5.

If one takes II and III to be the most likely intermediate biradicals involved in paths (a) and (b) [or (a′) and (b′)], respectively, then the predicted activation energies would be (in kJ mol^{-1}) $E_a \geqslant 225.5$, $E_b \geqslant 217.6$, $E_{a'} \geqslant 224.5$ and $E_{b'} \geqslant 216.6$. Whilst these values would be compatible with the observed activation energies, the differences $E_a - E_b$ and $E_{a'} - E_{b'}$ are small positive values and close to zero taking into account the likely errors in these calculations. The observed activation energy differences are much larger with $E_b > E_a$ and $E_{b'} > E_{a'}$. A similar situation occurs in the comparison of estimated and observed activation energies for the thermolysis of 2,2-dimethyloxetane.[1] Here it was concluded that it was impossible to reconcile the biradical mechanism with the observed Arrhenius parameters for the two paths. Frontier-orbital theory arguments suggest that the concerted path producing isobutene from 2,2-dimethyloxetane is favoured over the concerted path to produce ethene. This arises largely because of the energy difference between the relevant orbitals (HOMO) of isobutene and ethene. Applying similar arguments to the thermolysis of 2,2,3,4-tetramethyloxetane, a preference for 2-methylbut-2-ene [path (a)] over but-2-ene [path (b)] would still be predicted for a concerted mechanism but would be smaller because there is less difference in energy between the HOMO of 2-methylbut-2-ene and but-2-ene than between the HOMO of isobutene and ethene. The product ratios observed for the two decompositions show that this is in fact the case. For the two geometric isomers of 2,2,3,4-tetramethyloxetane it is found that the ratio R is greater for thermolysis of the *trans* compound than for thermolysis of the *cis* compound.

Similar observations were made by Imai and Nishida[10, 11] for the thermolysis of 3-alkyl-2-phenyloxetanes and related compounds in solution. These authors also inferred that the 'b'-type decomposition has a higher energy of activation than the 'a'-type decomposition for the compounds studied. They suggested that the thermolyses occur by concurrent biradical [path (b)] and concerted [path (a)] processes.

The same explanation would fit the results observed here, with the major pathway to 2-methylbut-2-ene and acetaldehyde occurring *via* a twisted $\sigma_{2s}+\sigma_{2a}$ activated complex. The Arrhenius parameters for path (b) are more in line with those expected for a biradical mechanism. In addition, the present compounds provide stereochemical evidence for the biradical mechanism for path (b), namely that the but-2-ene produced is formed from each isomer with partial retention of configuration which is consistent with a biradical intermediate of a lifetime sufficient to undergo some rotation but not producing complete equilibration. The observation that the ratio *cis*-but-2-ene/*trans*-but-2-ene formed from the *cis* reactant shows some temperature dependence whereas the comparable ratio from the *trans* reactant is independent of temperature in the range 410–490 °C (see fig. 3) is difficult to explain in terms of homogeneous biradical paths. However, the decomposition of the *cis* compound showed some evidence for a surface reaction which apparently produces relatively more *trans*-but-2-ene. [The value of r is significantly lower for decomposition of the *cis* reactant in the packed vessel (see table 3)]. It would be expected that a surface reaction would become relatively less important at higher temperatures producing an increased *cis*-but-2-ene/*trans*-but-2-ene ratio. Further experiments would be necessary to test this explanation quantitatively.

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(PAPER 3/1156)