# Substituent Effects on the Competing Thermal Cracking and Isomerization of Dimethyl Cyclobutane-1,2-dicarboxylates

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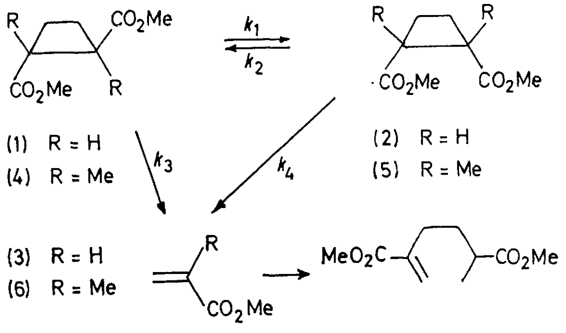
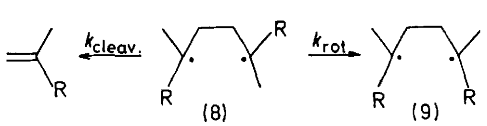
*Summary* The ratio of the rate constants for the thermal cracking and isomerization ($k_c/k_i$) of dimethyl cyclobutane-1,2-dicarboxylates and dimethyl 1,2-dimethylcyclobutane-1,2-dicarboxylates is 3—4 and $> 200$, respectively, indicating that, depending on substitution, even minimal stereochemical losses need not attend pyrolytic cycloreversions of cyclobutanes.

Stephenson and his co-workers have reported[1] high stereospecificity in the excited singlet state photoelimination of methyl 3,4-dimethyl-6-oxoheptanoate diastereoisomers (**11**). On the basis of these and other data, Stephenson and Brauman[2] suggested that putative singlet diradicals, intermediates postulated for photolytic azo-compound decomposition and for the Norrish Type II reaction, give products with anomalously high stereospecificity so that their behaviour is more consistent with that of a vibrationally excited species than with the model of a thermally equilibrated diradical intermediate (energy surface secondary minimum). This 'hot diradical' proposal, less conventional than the interpretation of spin correlation effects based on the lifetimes of singlet and triplet species alone,[3] depends heavily on the assumption that the properties of thermally equilibrated diradicals are most apparent in the pyrolysis of cyclobutanes (and in the behaviour of photochemically derived triplet intermediates) which give products with low stereospecificity. Since one recent report[4] showed that stereochemical losses in one case need not attend thermal cyclobutane fragmentations (indicating that perhaps very high barriers to internal rotation for diradicals with particular substitution are responsible for high stereospecificities) and since a reinterpretation of the Stephenson–Brauman proposal appeared[5] which takes into account very high barriers to rotation in singlet diyls, we have attempted to establish on a more quantitative basis the factors governing stereoretention in presumed diradicals by recognizing the 'ponderal' and electronic (delocalization) effects possible in the substitution pattern at radical centres for a series of butane-1,4-diyls. We report the pyrolytic behaviour of the isomeric dimethyl cyclobutane-1,2-dicarboxylates (**1**) and (**2**), the most readily isomerizable pair of simple cyclobutanes yet reported, and their 1,2-dimethyl derivatives (**4**) and (**5**).



When 50% solutions of (**1**) or (**2**) in diphenyl ether were pyrolysed at 330° in aged Pyrex ampoules, the isomeric cyclobutanes and methyl acrylate (**3**) were obtained as the only volatile products. Reasonably good first-order rates for interconversion and cracking (330°) could be determined by g.l.c. ($Ph_2O$ internal standard) at conversions of cyclobutane up to 20% for (**1**) and 30% for (**2**). Cracking was monitored by total disappearance of cyclobutane (minus isomerization) since under the conditions methyl acrylate polymerized at a moderate rate. The derived rate constants are: $k_1 = 3{\cdot}8 \pm 1{\cdot}0 \times 10^{-6}$, $k_2 = 7{\cdot}0 \pm 1{\cdot}0 \times 10^{-6}$, $k_3 = 1{\cdot}0 \pm 0{\cdot}4 \times 10^{-5}$, and $k_4 = 2{\cdot}7 \pm 0{\cdot}5 \times 10^{-5}\ s^{-1}$. The desired ratio of the rate constants which reflects stereochemical loss, $k_c/k_i$ ($k_3/k_1$ and $k_4/k_2$), relates rates of cracking and isomerization (measures 'stereoretention,' *vide infra*). This ratio could be directly and more precisely determined from g.l.c. analysis of olefin and isomer produced on pyrolysis in a quartz flow system which minimized secondary pyrolysis (contact time 5—10 s). Thus, $k_c/k_i = 3{\cdot}1 \pm 0{\cdot}6$ for (**2**) (420°) and $4{\cdot}4 \pm 0{\cdot}8$ for (**2**) (402°) at conversions of 5—9% and 8—10%, respectively.

The dimethyl-dicarboxylates (**4**) and (**5**) gave on pyrolysis (30% solutions in $Ph_2CH_2$ at 270°) methyl methacrylate (**6**) and an olefin (**7**). The latter was shown not to be a primary pyrolysis product since the conversion (**6**) → (**7**)[6] proceeded moderately and a plot of the product ratio (**7**):(**8**) *vs.* percentage conversion of cyclobutane passed through the origin ($\pm 0{\cdot}05$) on extrapolation. Significantly, during the pyrolyses of the cyclobutanes (**4**) or (**5**), isomerization could not be detected (n.m.r.) over a range of conversions up to 90%. However, g.l.c. analysis of the pyrolysates at high conversion consistently showed traces of the isomeric cyclobutane, and the lower limit to the ratio $k_3/k_1$ ($k_4/k_2$) was estimated, conservatively, to be 200. The rates of cracking (n.m.r.; $Ph_2CH_2$ internal standard) were smoothly first-order (3 half-lives): $k_3 = 4{\cdot}30 \pm 0{\cdot}21 \times 10^{-4}$; $k_4 = 1{\cdot}96 \pm 0{\cdot}10 \times 10^{-4}\ s^{-1}$ (270°).



We emphasize that the partitioning of a 1,4-diradical [*e.g.* (**8**)] among bond rotation, cleavage, and closure will be strongly affected by the pattern of substitution at the radical centres and that it is by no means general that cyclobutanes lose their particular stereochemical arrangement on cracking (see Table). Measurements of phenomenological 'stereoretention' in diradicals (values calculated easily from product distribution data) are best related to the ratio $k_{cleave}/k_{rot}$ for Type II photoelimination and cyclobutane decomposition. Since 1,4-diradical systems only rarely reach stereoequilibrium before decomposition, it seems likely that processes that require the achievement of several (rotation) barriers (either step-wise or simultaneously) would not compete effectively with simple cleavage or closure. Noticeably, a 'ponderal' effect[7] obtains upon terminal replacement of hydrogen by other groups for each pair of similar structures. This has already been pointed out in the photoelimination of (**10**).[8] In addition, comparison *among the pairs* of cyclobutanes (R = H) [*e.g.*, (**1**), (**12**), (**14**)] reveals an electronic effect most probably related to the diffuseness of unpaired electron density (which would

| Diradical precursor | Temp. ($t$/°C) | Stereo-retention[a] | Ref. |
|---|---|---|---|
| Type II photoelimination | | | |
| (**10**) | Room temp. | 9—19 | 8a |
| (**11**) | ,, ,, | 90 | 1 |
| Cyclobutane pyrolysis | | | |
| (**12**) | 401 | 4—8 | 10 |
| (**13**) | 401 | ⩾22 | 4 |
| (**1**) and (**2**) | 402 | 3—4 | This work |
| (**4**) and (**5**) | 270 | ⩾200 | ,, ,, |
| (**14**) | 139 | 0·14[b] | 11 |
| (**15**) | 136 | 2·1[b] | 12 |

[a] For Type II reaction, ratio of stereospecific to nonstereospecific olefin product. For the cyclobutanes: $k_c/k_i$. Range indicates measurements for two isomers. [b] *trans*-Cyclobutane only, appearance of *cis* measured as Cope product.

tend to slow down cleavage) in diradicals increasingly stabilized by delocalization.[9]

$MeC(:O)CH_2CHMeCHMeR$

(10) $R = D$
(11) $R = CH_2CO_2Me$

(12) $R^1 = Me$; $R^2 = H$
(13) $R^1 = Me$; $R^2 = CD_3$
(14) $R^1 = CH_2{:}CH$; $R^2 = H$
(15) $R^1 = CH_2{:}CH$; $R^2 = Me$

It appears therefore that the earlier[2] assignment of differential behaviour in singlet diradicals derived from **(11)** (photochemically) and **(12)** (thermally) to the intermediacy of vibrationally excited diradicals [for **(11)**] may have been unnecessary and the results may have been based circumstantially on the mechanical properties of the various substituted diyls. This is not to say that intermediates of the same type derived by photochemical and thermal means should be expected to behave identically, rather that the data for 1,4-diradicals can so far be accommodated without the proposal of vibrationally hot species in solution.

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