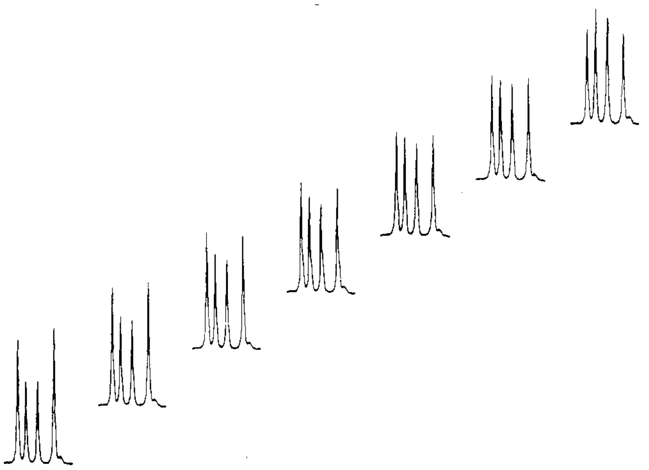
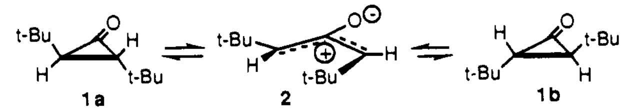
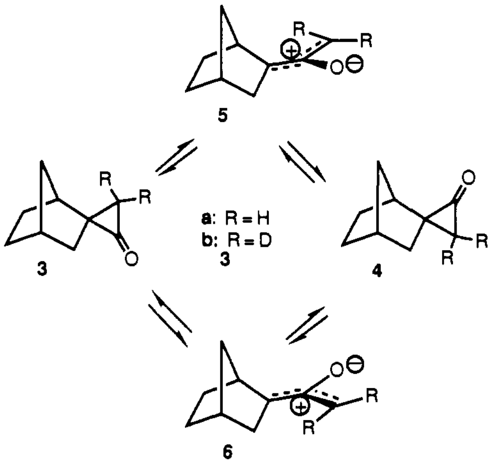


Figure 1. ^2H NMR spectra showing the equilibration of **3b** (outer pair of peaks) and **4b** (inner pair). Each spectrum spans the range 1.8–0.9 ppm.

Scheme I



Scheme II



constant for the forward reaction **3** → **4** can be defined in terms of the forward rate constants for the two component pathways as $k_f = k_5 + k_6$. Although the present experiments do not permit a separation of k_5 and k_6, the *minimum value* for the faster of the two is $k_f/2$. Whether the oxyallyls **5** and **6** are assumed to be transition states or metastable intermediates,[9] the *maximum value* of the free energy separation at 246.6 K between the reactant cyclopropanone **3** and the oxyallyl on the favored pathway for its stereomutation is $\Delta G^‡ = -RT[\ln (k_f/2) - \ln (RT/Nh)] \leq 19.1$ kcal/mol in diethyl ether (NMR method). The present finding that cyclopropanone–oxyallyl interconversion can occur at low temperature carries mechanistic implications for the nature of the intermediates in the Favorski rearrangement.[10]

We have found a strong solvent dependence of the rate of stereomutation. Anticipating the completion of a detailed study, we offer here comparative half-lives for the k_{obsd} process of about 80 min at 244 K in diethyl ether and at 195 K in dichloromethane.

Arrhenius activation parameters (values by GC and NMR methods) for the equation $\log k_f = \log A - (E_a/2.3RT)$ in diethyl ether were $E_a = 16.3 \pm 1.3$ and 15.3 ± 1.4 kcal/mol and $\log A = 10.4 \pm 1.4$ and 9.6 ± 1.4 (A in s^{-1}). The origin of the low A value is under study.

At 353 K, $\Delta G^‡$ for the stereomutation of *trans*-2,3-di-*tert*-butylcyclopropanone, 27.4–29.2 kcal/mol in five solvents,[1,11] is 7–9 kcal/mol greater than that for **3**. Differences in the structure and position of the substituents may contribute electronic and/or bond angle strain components to this increment, but it seems likely that the dominant factor is steric strain in the transition state. The putatively disrotatory thermal ring opening creates a large 1,3-allylic interaction in the oxyallyl of the di-*tert*-butyl system.

The present experiments thus suggest that the barrier for opening of a relatively unhindered dialkylcyclopropanone is remarkably low. Its magnitude provides a calibration point for future theoretical studies.

Acknowledgment. We thank the National Science Foundation for partial support of this work and for a graduate fellowship to M.H.J.C. This work was also supported in part by the National Institute of General Medical Sciences.

Supplementary Material Available: Listings of details of syntheses and characterizations (10 pages). Ordering information is given on any current masthead page.

---

(9) (a) We find that the cycloaddition of **3** and **4** to conjugated dienes (cyclopentadiene, furan, 6,6-dimethylfulvene) requires temperatures at least as high as those required for **3** → **4** stereomutation. This is consistent with, but insufficient to prove,[9b-d] the intermediacy of oxyallyl intermediates in the addition reaction. (b) Cf. Turro, N. J.; Hammond, W. B. *Tetrahedron* **1968**, *24*, 6017. (c) Turro, N. J.; Edelson, S. S.; Williams, J. R.; Darling, T. R.; Hammond, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 2283. (d) Edelson, S. S.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 2770.

(10) Reviews: (a) Hunter, D. H.; Stothers, J. B.; Warnhoff, E. W. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 437 ff. (b) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, 2nd ed.; McGraw-Hill: New York, 1977; pp 991 ff.

(11) Since the rate constant for enantiomerization of **1** is $k_{rac}/2$, and since the symmetry number of the reactant ($\sigma = 2$) differs from that of its transition state ($\sigma = 1$), we have calculated[11b] $\Delta G^‡$ for enantiomerization as $-RT[\ln (k_{rac}/(2 \times 2)) - \ln (RT/Nh)]$. (b) Pollak, E.; Pechukas, P. *J. Am. Chem. Soc.* **1978**, *100*, 2984.

Computer Software Reviews

MacFormula, Version 3.11. JED Software: 3857 MacGregor Common, Livermore, California 94550. List Price: $29.00 plus $3.00 shipping in US, $5.00 foreign. (Upgrade from prior versions available by returning disk with $3.00 for shipping and handling.)

MacFormula is a very simple program for the Macintosh for calculating molecular weights, stoichiometry, and elemental analysis data.

Once one gets past the title screen, the main window is shown. It has exactly two boxes to enter data. The first is for any molecular formula. The box is highlighted with the message "Enter Formula Here" at the start. One types any formula, using element symbols and numbers (which are not subscripted). Then clicking in the second box (or using the tab key, a useful feature for mouse phobes) lets one enter a number of milligrams. The average mass, the exact mass, and the number of millimoles are displayed, as well as percentage composition of each element present. If one clicks on the word "milligrams" it toggles to millimoles. One has to click on the "calculate" button or hit "Enter" to get the new calculation.

Data for the entire periodic table are programmed in, and one can enter some user-chosen values (i.e. for isotopes). Extra molecular fragments (such as waters of hydration) and fractional molecular formulas can also be accommodated and common abbreviations for molecular fragments, such as Ph = phenyl, can be used. The entire dictionary of elements and fragments that are recognized can be printed to a printer (it would be useful to be able to print them on screen also).

MacFormula runs on any Macintosh and can be run in the background with system 7. It is a simple but very useful program, especially to have on a computer in the lab.

John N. Marx, *Texas Tech University*