motion in the opening and reclosure of a 0,0 trimethylene. In the absence of an alternative rationale, the results may be viewed as confirmation of a remarkable theoretical prediction.

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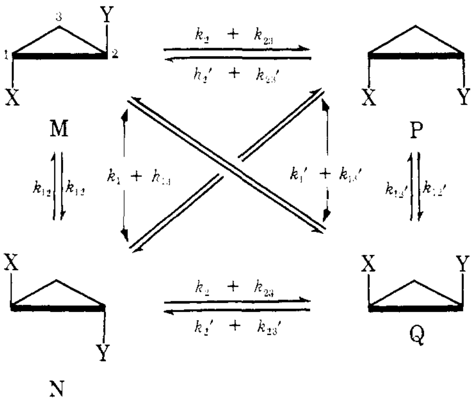
Synchronous Double Rotation in the Stereomutation of Optically Active 1-Phenylcyclopropane-*2-d*[1]

Sir:

A recent study[2] of the minimally perturbed case of *trans*-cyclopropane-*1,2-d*$_2$ has confirmed the prediction[3] that stereomutation of cyclopropane should occur by synchronous rotation of two methylene groups. However, previous studies with a variety of cyclopropanes bearing true rather than isotopic substituents have failed to detect this process.[4-10] Although the theoretical calculations[3,11] have dealt only with cyclopropane itself, one might have hoped for a broader range of applicability of the results. Unless the predicted effect is substantial enough to survive minor structural changes in the substrate, there is reason to question whether the underlying theoretical basis has been identified properly. The present paper reports that a synchronous double rotation also is prominent in the stereomutation of 1-phenylcyclopropane-*2-d*.

Scheme I



Scheme I outlines a generalized version of an experimental system common to several of the previous studies, where X or Y are alkyl, alkenyl, phenyl, CO_2Me, CN etc.[6,7,9,10] It involves an unsymmetrically 1,2-disubstituted cyclopropane, in which both the trans and cis isomers are chiral. Six independent phenomenological rate constants characterize the network of epimerizations and enantiomerizations.

The most general analysis of Scheme I would permit any of the three ring carbons and their attached substituents to be involved in both unaccompanied single rotations (with single index mechanistic rate constants) and synchronous double rotations (with double index rate constants).[12] Note that single rotation of the unlabeled carbon C_3 results in no reaction.

For the special case of chiral 1-phenylcyclopropane-*2-d* (M, X = Ph; Y = D), the molecular symmetry would require that, to a very close approximation, all of the primed rate constants of Scheme I become equal to their unprimed counterparts, since the relevant kinetic isotope effects would be negligibly different from 1.00. Moreover, there is a unique benefit conferred by the symmetry in that the rate constant k_{13} for double rotation of C_1–C_3 is necessarily equal to the rate constant k_{12} for double rotation of C_1–C_2, modified by the isotope effect. The latter now might not be negligible and should lie in the range 1.00–1.10.[2] Thus, $k_{13} = k_{12}k_H/k_D$.

If k_1 has a finite value, the pyrolysis would include a contribution from single rotation of C_1, either in a Smith mechanism[13] or in a trimethylene biradical.[14] On the other hand, if $k_1 = 0$, the interconversions M $\rightleftharpoons$ Q and N $\rightleftharpoons$ P would be entirely characterized by the double rotation rate constant k_{13}. The problem thus reduces to devising an experimental estimate of the magnitude of k_1.

Conversion of (−)-*trans*-2-phenylcyclopropanecarboxylic acid (M, X = Ph; Y = CO_2H; configuration as shown[15]) to the nitrile and epimerization of the latter with KO-*t*-Bu-DMSO give a mixture of nitriles M and P (X = Ph, Y = CN), which after separation and treatment with PhMgBr gives ketones M and P (X = Ph, Y = COPh) of identical

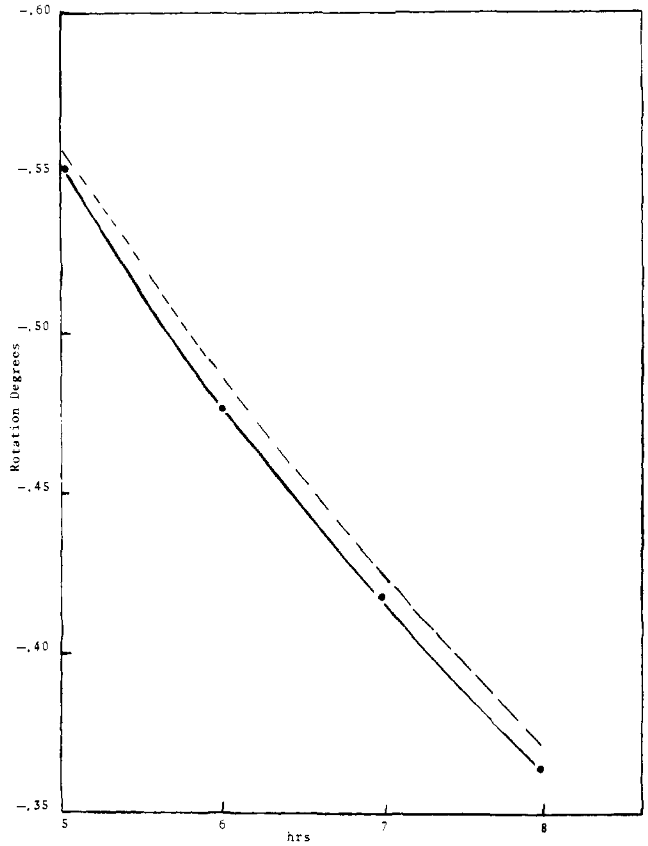


Figure 1. Loss of optical activity in the pyrolysis of (−)-*trans*-1-phenylcyclopropane-*2-d*. Only the later kinetic points are shown, ● experimental points. Both curves are calculated using $k_H/k_D = 1.10$. The dashed curve is for $k_1 = 0.395 \times 10^{-5}$ sec^{-1}; the solid one is for $k_1 = 0$.

optical purity (96.3%). Column chromatographic separation and treatment of the trans ketone with $NaND_2$ in benzene give a sample (M′) of 1-phenylcyclopropane-*2-d* which is 98.9% trans and 1.1% cis by infrared analysis, α_{365} + 1.212° (neat). Similar treatment of the cis ketone gives a sample (P′) of 1-phenylcyclopropane-*2-d* which is 40% trans and 60% cis. Appropriate portions of samples M′ and P′ are combined to produce a mixture containing 50% each of *trans*- and *cis*-1-phenylcyclopropane-*2-d*, each of which is at identical optical purity. This mixture (MP) is at chemical equilibrium but not at enantiomeric equilibrium.

Gas phase pyrolysis of a sample of M′ or its enantiomer (two separate runs) at 309.5 ± 0.5° and 710 Torr causes loss of optical activity and isomerization to a trans-cis equilibrium mixture.[16] The polarimetric reaction is not first order, because the trans and cis isomers have different optical rotatory powers. The isomerization, however, is cleanly first order with rate constant

$$k_i = -(1/t)\ln\left[(T - C)/(T_0 - C_0)\right] = 2.48 \times 10^{-5}\ \text{sec}^{-1}$$

It can be shown that

$$k_i = 2(k_2 + k_{23} + k_1 + k_{13})$$

Gas phase pyrolysis of the synthetic chemical equilibrium mixture MP under the same conditions produces no change in trans-cis isomer composition but results merely in first-order decline of optical activity with rate constant

$$k_\alpha = (1/t)\ln(\alpha_0/\alpha) = 4.06 \times 10^{-5}\ \text{sec}^{-1} = 2(k_{12} + k_1 + k_{13})$$

These data fix the relationships of eq 1-3.

$$k_\alpha - k_i = 2(k_{12} - k_2 - k_{23}) = 1.58 \times 10^{-5}\ \text{sec}^{-1} \quad (1)$$

$$k_{12} \geqq 0.79 \times 10^{-5}\ \text{sec}^{-1} \quad (2)$$

$$k_\alpha/2 = k_{12} + k_1 + k_{13} = 2.03 \times 10^{-5}\ \text{sec}^{-1} \quad (3)$$

Substituting for k_{13} its symmetry-equivalent $k_{12}k_H/k_D$, we rewrite eq 3 as

$$k_1 = 2.03 \times 10^{-5}\ \text{sec}^{-1} - k_{12}(1 + k_H/k_D)$$

From the lower limit $k_{12} \geqslant 0.79 \times 10^{-5}$ sec^{-1} and the range of isotope effects $1.00 \leqslant k_H/k_D \leqslant 1.10$, it follows that the upper limit for k_1 lies between 0.37×10^{-5} and 0.45×10^{-5} sec^{-1}. Thus, k_1, which measures the rate of unaccompanied single rotation of C_1, represents not more than 18-22% of the total reaction in which C_1 rotates ($k_1 + k_{12} + k_{13}$). At least 78-82% of the process occurs by the synchronous double rotation measured by $k_{12} + k_{13}$.

A more accurate estimate may be obtained by an analysis of the polarimetric kinetics in the pyrolysis of sample M′. From the relative rotations of the trans and cis isomers at equal enantiomeric purity, one can calculate the optical rotation corresponding to any mixture of trans and cis. Experiment fixes the already described relationships among k_1, k_2, k_{12}, k_{13}, and k_{23} (eq 1-3). The kinetics of Scheme I then may be fitted[17] by using k_1 and the isotope effect as adjustable parameters. For each value of k_H/k_D, there is a corresponding best fit value for k_1 (rms error of 0.00074° in α). Values of k_H/k_D = 1.00, 1.10, and 1.20 give best fit k_1 values of 0.098×10^{-5}, 0, and -0.095×10^{-5} sec^{-1}, respectively. This brackets the permissible values of k_1 into a small range near zero. Figure 1 shows that when k_1 is chosen outside this range but near the previously defined upper limit, the fit is clearly worse. On the assumption that $k_H/k_D \geqslant 1.00$, no more than about 4% of C_1 stereomutation can occur by single rotation. Thus, the major pathway is a reaction in which every rotation of CHPh is accompanied by a synchronous rotation of CH_2 or CHD.

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Photochemistry of Carbonyl Compounds through the Enol Form. Involvement of a Cyclopropanone Intermediate in the Photorearrangement of 4-Carbomethoxy-3-chromanone[1]

Sir:

Although the photochemical behavior of the carbonyl group has received much scrutiny in the past decade,[2,3] relatively little is known about the photochemistry of the small amount of enol tautomer which exists in equilibrium with the keto form.[4] In an earlier report[5] dealing with the photorearrangement of 4-phenyl-3-chromanone (**1**) to 4-phenyldihydrocoumarin (**2**),[6] evidence was presented which demonstrated that the enol content can be an overriding factor in determining the quantum efficiency of a photoreaction. As part of our continuing studies dealing with enol photochemistry,[7,8] we have undertaken an investigation of the excited state behavior of the 4-carbomethoxy-3-chromanone (**3**) system. We now report that in extending our studies to this system, we have discovered an unusual solvent effect which controls the product distribution. In addition, we have uncovered an unprecedented photodecarbonylation reaction which can best be explained by invoking the intermediacy of a transient cyclopropanone.

Using procedures similar to those descried for the preparation of other chromanones,[9] 4-carbomethoxy-3-chromanone (**3**), mp 35–36°, was prepared in high yield. The nmr spectrum of **3** indicates that this β-ketoester exists predominantly (>98%) in the enol form (τ 5.98 (*s*, 3 H), 5.24 (*s*, 2 H), 2.0–3.1 (*m*, 4 H), and −3.0 (*s*, 1 H, exchanged with D_2O)). When a thoroughly deaerated methanolic solution of **3** was treated with sodium methoxide and then irradiated with light of wavelength >300 nm,[10] an extremely rapid and clean conversion to methyl 3-(*o*-hydroxyphenyl)-3-carbomethoxypropanoate (**4**), mp 101–102°, was observed. The identity of **4** was determined by its straightforward spectral characteristics (nmr (100 MHz), τ 7.26 (dd, 1 H, J = 16.0 and 7.0 Hz), 6.68 (dd, 1 H, J = 16 and 9.0 Hz), 6.32 (s, 3 H), 6.28 (s, 3 H), 5.70 (dd, 1 H, J = 9.0 and 7.0 Hz), 2.6–3.3 (m, 4 H)) as well as its facile conversion to 4-carbomethoxydihyrocoumarin (**5**), mp 79–80°, on heating in the presence of a trace of acid. The structure of dihydrocoumarin **5** (nmr (100 MHz), τ 7.18 (dd, 1 H, J = 17.0 and 6.0 Hz), 6.84 (dd, 1 H, J = 17.0 and 3.0 Hz), 6.28 (s, 3 H), 6.05 (dd, 1 H, J = 6.0 and 3.0 Hz), 3.0–3.6 (m, 4 H)) was established by comparison with an independently synthesized sample.

Irradiation of **3** in acetonitrile at 25° for 14 hr under a nitrogen atmosphere with Pyrex-filtered light gave a 3:1 mixture of 4-carbomethoxydihydrocoumarin (**5**) and *o*-hydroxy-α-carbomethoxystyrene (**6**) (Scheme I). The two components could be easily separated by thick-layer chromatography. Elemental analysis, the ultraviolet spectrum (methanol, 295, 263, 252, and 243 nm (ϵ 4700, 4700, 6300, and 6500)), and the nmr spectrum (100 MHz, τ 6.12 (s, 3 H) 4.05 (d, 1 H, J = 1.2 Hz), 3.55 (d, 1 H, J = 1.2 Hz), 2.70–3.20 (m, 4 H), and 2.50 (s, 1 H, exchanged with D_2O)) suggested *o*-hydroxy-α-carbomethoxystyrene (**6**), mp 76–77°, as the structure of the minor photoproduct. Chemical confirmation was obtained by (a) catalytic reduction to methyl 2-(*o*-hydroxyphenyl)propanoate (**7**) and (b) conversion to *o*-methoxy-α-carbomethoxystyrene (**8**), which was, in turn, independently synthesized. It is interesting to note that when the irradiation of **3** was carried out

Scheme I