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Mendeleev Commun., 2004, 14(6), 297–299

Mendeleev
Communications

The photochemistry of optically active (*E*)-cyclooctene: lamp *versus* laser

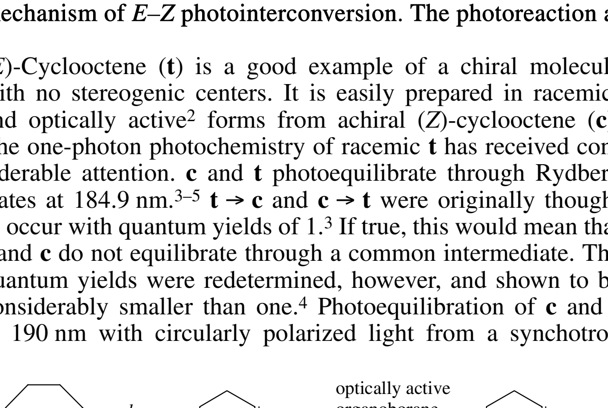
Fang Gao,[a] Run-hua Li,[b] Robert N. Compton[a,b] and Richard M. Pagni*[a]

[a] *Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA. E-mail: rpagni@utk.edu*
[b] *Department of Physics, University of Tennessee, Knoxville, TN 37996, USA*

DOI: 10.1070/MC2004v014n06ABEH002012

The photochemistry of optically active (*E*)-cyclooctene in cyclopentane was initiated with a lamp at *ca.* 254 nm and a Nd-YAG laser at 266 nm. The alkene racemizes slightly faster than it isomerizes to (*Z*)-cyclooctene, suggesting a previously hidden mechanism of *E*–*Z* photointerconversion. The photoreaction at 266 nm may be multiphoton in character.

(*E*)-Cyclooctene (**t**) is a good example of a chiral molecule with no stereogenic centers. It is easily prepared in racemic[1] and optically active[2] forms from achiral (*Z*)-cyclooctene (**c**). The one-photon photochemistry of racemic **t** has received considerable attention. **c** and **t** photoequilibrate through Rydberg states at 184.9 nm.[3–5] **t** → **c** and **c** → **t** were originally thought to occur with quantum yields of 1.[3] If true, this would mean that **t** and **c** do not equilibrate through a common intermediate. The quantum yields were redetermined, however, and shown to be considerably smaller than one.[4] Photoequilibration of **c** and **t** at 190 nm with circularly polarized light from a synchotron source yields **t** with a very small enantiomeric enrichment.[6] Chiral sensitizers, however, are much more effective in generating **t** with large enantiomeric enrichment.[7]



c

racemic **t**

optically
active **t**

We report here the results on the photolysis of (–)-**t**[†] in degassed cyclopentane initiated with a lamp[‡] and the fourth harmonic from a Nd-YAG laser at 266 nm. **c** and **t** have absorption maxima in cyclopentane at 198 ($\varepsilon = 6.3\times10^3$ dm^3 mol^{-1} cm^{-1}) and 200 nm ($\varepsilon = 4.9\times10^3$ dm^3 mol^{-1} cm^{-1}), respectively, and each absorption profile tails to at least 250 nm. The decay of **t** was

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[†] Racemic (*E*)-cyclooctene was prepared in about 20% yield by the photolysis of a degassed mixture of (*Z*)-cyclooctene and Cu_2Cl_2 in a quartz tube using 253.7 nm lamps in a Rayonet reactor.[1] (*E*)-Cyclooctene was resolved by treatment of the racemic olefin with a deficiency of (–)-*sym*-tetraisopinocamphenyldiborane as described by Water.[2] This afforded the (–)-enantiomer in close to 20% optical purity.

[‡] Rayonet Reaction consisting of 4 2537 Å lamps, 35 W per lamp. The low pressure lamps generate most of its light at 253.7±5 nm, with a very small amount of light down to the *ca.* 220 nm.

Table 1 Photolysis of (–)-**t** in cyclopentane.[a]

Lamp			Laser		
Time/h	$(\mathbf{t}_R + \mathbf{t}_S)/\mathbf{t}_{R_0}$	$(\mathbf{t}_R - \mathbf{t}_S)/\mathbf{t}_{R_0}$	Time/min	$(\mathbf{t}_R + \mathbf{t}_S)/\mathbf{t}_{R_0}$	$(\mathbf{t}_R - \mathbf{t}_S)/\mathbf{t}_{R_0}$
0	1	1	0	1	1
0.25	0.980	0.964	10	0.962	0.956
0.50	0.942	0.922	20	0.900	0.890
1.00	0.879	0.854	30	0.836	0.820
1.50	0.828	0.808	40	0.767	0.744
2.00	0.766	0.748	50	0.692	0.666
3.00	0.683	0.660	60	0.612	0.588
4.00	0.591	0.576	80	0.430	0.408
5.00	0.512	0.496			

[a] $\mathbf{t}_R$ = (–)-enantiomer; $\mathbf{t}_S$ = (+)-enantiomer; $\mathbf{t}_{R_0}$ = initial amount of $\mathbf{t}_R$.

followed as a function of time by gas chromatography/mass spectrometry[§] and the racemization of (–)-**t**, by polarimetry.[¶] As shown in a different case,[8,9] comparison of decay and racemization of a substrate provides valuable mechanistic information.

The results of the lamp photolysis are shown in Table 1 (columns 1–3), where $\mathbf{t}_{R_0}$ is the initial amount of the (–)-enantiomer, $(\mathbf{t}_R + \mathbf{t}_S)/\mathbf{t}_{R_0}$ is the normalized total amount of **t**, and $(\mathbf{t}_R - \mathbf{t}_S)/\mathbf{t}_{R_0}$ is the normalized difference in the amounts of the two enantiomers. Under these circumstances, about half the starting material is gone in 5 h. It is also apparent that the substrate racemizes slightly faster than it is converted into **c**. To interpret these results, plots of $\ln[(\mathbf{t}_R + \mathbf{t}_S)/\mathbf{t}_{R_0}]$ and $\ln[(\mathbf{t}_R - \mathbf{t}_S)/\mathbf{t}_{R_0}]$ *versus* time were made, yielding $\ln[(\mathbf{t}_R + \mathbf{t}_S)/\mathbf{t}_{R_0}] = -0.114\,(\text{time}) + 0.0075$ (correlation coefficient of 0.9991) and $\ln[(\mathbf{t}_R - \mathbf{t}_S)/\mathbf{t}_{R_0}] = -0.138\,(\text{time}) + 0.0073$ (correlation coefficient of 0.9993). It is the ratio of the slope of the first straight line to that of the second which has mechanistic relevance: 0.96±0.01, a value a little less than one. This suggests that $\mathbf{t}_R$ racemizes slightly faster than it is converted into **c**.

To assess the significance of the ratio of slopes, it is necessary to consider the manner in which the cyclooctene isomers interconvert photochemically. Based on the structures of $\mathbf{t}_R$ and $\mathbf{t}_S$, the two enantiomers of **t**, and **c** and the extensively studied *cis–trans* isomerization of acyclic alkenes,[10] the reactions in equation (1) may be assumed to operate.

$$\mathbf{t}_R \rightleftharpoons \mathbf{c} \rightleftharpoons \mathbf{t}_S \tag{1}$$

The mechanism in equation (1) may be expanded because photochemically induced *cis–trans* isomerization proceeds through intermediates in which the ends of the C–C double bond are perpendicular to one another.[10] In the case of cyclooctene, the perpendicular intermediate is chiral and exists in enantiomeric forms, $\mathbf{p}_R$ and $\mathbf{p}_S$. This yields equation (2), in which k_1 and k_2 represent the photochemical steps whose details can be found elsewhere[11] and k_{-1} and k_{-2} represent the rate constants for the chiral intermediates to reform $\mathbf{t}_R$, $\mathbf{t}_S$, and **c**.

$$\mathbf{t}_R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{p}_R \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \mathbf{c} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{p}_S \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathbf{t}_S \tag{2}$$

If $\mathbf{t}_R = \mathbf{t}_{R_0}$ and $\mathbf{t}_S = \mathbf{c} = 0$ at time = 0, the conditions used in the experiments, equation (2) yields the following time-dependent results provided the photochemical steps (k_1, k_2) are also first-order in substrate.

$$\mathbf{t}_R - \mathbf{t}_S = \mathbf{t}_{\mathrm{R}_0}\exp(-k_1F\mathbf{t}); \tag{3}$$

$$\mathbf{t}_R + \mathbf{t}_S = \frac{2k_2(1-F)\mathbf{t}_{R_0}}{k_1F + 2k_2(1-F)} + \frac{k_1F\mathbf{t}_{R_0}}{k_1F + 2k_2(1-F)}\exp\{-[k_1F + 2k_2(1-F)]\mathbf{t}\}, \tag{4}$$

where $F = k_{-2}/(k_{-1} + k_{-2})$, the fraction of the time that $\mathbf{p}_R$ or $\mathbf{p}_S$ yields **c**. The plot of $\ln[(\mathbf{t}_R - \mathbf{t}_S)/\mathbf{t}_{R_0}]$ *versus* time will be linear, as observed in the experiment. The similar plot of $\ln[(\mathbf{t}_R + \mathbf{t}_S)/\mathbf{t}_{R_0}]$ will not be linear. If $F \approx 1$, however,

$$\mathbf{t}_R + \mathbf{t}_S \approx \mathbf{t}_{\mathrm{R}_0}\exp\{-[k_1F + 2k_2(1-F)]\mathbf{t}\}; \tag{5}$$

The plot of $\ln[(\mathbf{t}_R + \mathbf{t}_S)/\mathbf{t}_{R_0}]$ *versus* time will thus be linear. The theoretical ratio of slopes then is $[k_1 + 2k_2(1-F)]/k_1F$, which will always be ≥ 1, a prediction not born out by the experiment. The ratio of slopes will be 1 of course when $F = 1$. Even if an alternate mechanism is invoked in which a carbene (cyclooctanylidene) connects the cyclooctenes, the ratio of slopes will still be ≥ 1.

$$\begin{tikzcd}
\mathbf{t}_R \arrow[r, shift left, "k_1"] & \mathbf{p}_R \arrow[l, shift left, "k_{-1}"] \arrow[rr, shift left, "k_3"] \arrow[dr, shift left, "k_{-2}"] & & \mathbf{p}_S \arrow[ll, shift left, "k_3"] \arrow[r, shift left, "k_{-1}"] \arrow[dl, shift left, "k_{-2}"] & \mathbf{t}_S \arrow[l, shift left, "k_1"] \\
& & \mathbf{c} \arrow[ul, shift left, "k_2"] \arrow[ur, shift left, "k_2"] & &
\end{tikzcd} \tag{6}$$

One manner in which to explain the results is to assume that the chiral intermediates not only interconvert through **c** but also directly. This yields the mechanism in equation (6), which yields the following time-dependent results:

$$\mathbf{t}_R - \mathbf{t}_S = \mathbf{t}_{R_0}\exp\left[-k_1\frac{F(k_{-1} + k_{-2}) + 2k_3}{k_{-1} + k_{-2} + 2k_3}\mathbf{t}\right]; \tag{7}$$

$$\mathbf{t}_R + \mathbf{t}_S \approx \mathbf{t}_{R_0}\exp\{-[k_1F + 2k_2(1-F)]\mathbf{t}\}. \tag{8}$$

Suitable logarithmic plots then yield the ratio of the slopes $\approx [F(k_{-1} + k_{-2} + 2k_3)]/[F(k_{-1} + k_{-2}) + 2k_3]$ provided that F is close to but less than 1.[††] This ratio is ≤ 1 when $F \le 1$. Setting the ratio of slopes equal to 0.96, the experimental value, one obtains after considerable rearranging $M = k_3/(k_{-1} + k_{-2} + k_3) = F/(48 - 49F)$, the fraction of $\mathbf{p}_R$ going to $\mathbf{p}_S$ and *vice versa*. Further mathematical manipulation yields N, the fraction of $\mathbf{p}_R$ or $\mathbf{p}_S$ going to **c**, and O, the fraction going to **t**. Table 2 shows a series of M, N, and O values obtained for a few large values of F. The mechanism in equation (6) thus requires a significant fraction of the chiral perpendicular intermediates to interconvert directly. Theoretical calculations on $\mathbf{p}_R$ and $\mathbf{p}_S$ and their interconversion will be required to validate this hypothesis.[‡‡]

Photolysis of the cyclooctenes at 266 nm, using the fourth harmonic of a Nd-YAG pulsed laser (10 Hz), proved equally interesting. At this wavelength, **t** and **c** have little or no absorption ($\varepsilon << 1$). Under these conditions, **c** is converted slowly into **t** and a small amount of cycloocta-1,3-diene while **t** is converted into **c** rapidly.[§§]

The results of the photochemistry of $\mathbf{t}_R$ in degassed cyclopentane are shown in Table 1 (columns 4–6). Approximately half of $\mathbf{t}_R$ is consumed in 1 h. As was the case of the lamp photolysis, $\mathbf{t}_R$ racemizes slightly faster than it disappears, suggesting that a mechanism similar to that observed for the lamp photolysis is occurring here. The data were initially analyzed in the same manner as the lamp data, yielding a ratio of slopes of 0.94±0.16. The ratio is very similar to that observed for the

Table 2 Partitioning of $\mathbf{p}_R$ into $\mathbf{p}_S$, $\mathbf{t}_R$, and **c**.

F	M	N	O
0.96	1	0	0
0.94	0.49	0.48	0.03
0.92	0.32	0.63	0.05
0.90	0.23	0.69	0.08

[§] Hewlett-Packard 6890 GC/5973 MSD with an HP-5MS column (cross-linked 5% PH ME siloxane); 30 m × 0.250 mm × 0.25 µm. **t** and **c** were baseline separated with this GC/MS system. GC experiments were carried out back to back to insure consistent and accurate readings.

[¶] Perkin-Elmer 241 Polarimeter with Na 589 lamp. Because **c** is the only product formed in the photoreaction, it is straightforward to convert polarimetry readings into extent of racemization.

[††] Photolysis of **t** and **c** at 184.9 nm yields a *trans*:*cis* ratio of 0.96 at the photostationary state.[12,13] This is consistent with the known molar absorption coefficients of **t** and **c** at this wavelength, as well as the quantum yields of **t** → **c** and **c** → **t**.[4] This implies that $F \sim 0.5$ at 184.9 nm, a value far different than implied here. Because different excited states are likely populated at 184.9 nm than the ones populated here, different mechanisms of isomerization may be operating.

[‡‡] $\mathbf{t}_R$ and $\mathbf{t}_S$ interconvert thermally ($\Delta H^{\neq} = 39.7$ kcal mol^{-1}; $\Delta S^{\neq} = 0$ cal K^{-1} mol^{-1}) without the intervention of **c**.[14]

[§§] One can also easily detect Raman scattering from the cyclooctene isomers under these conditions.

lamp photolysis of $\mathbf{t}_R$ but the standard deviation is very large. The two log plots in fact generate curved rather than straight lines. The most likely explanation for why the log plots are not linear is that with the high powered pulsed laser the conditions necessary to make the photochemical steps first-order in substrate concentration – low absorbance by the solution – do not hold.[11]

In conclusion, we have shown that the *cis–trans* isomerization of **t** and **c** may be more complicated than previously suspected. A plausible, but by no means exclusive, explanation is that the chiral perpendicular intermediates interconvert directly. Another possibility is that two mechanisms of isomerization, *e.g.*, the one described in equation (2) and the one involving the carbene cyclooctanylidene, occur simultaneously. Further experimental and theoretical research will be required to test these hypotheses.

This work was supported by the National Science Foundation.

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Received: 10th August 2004; Com. 04/2337