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Stereochemical Studies on an α-Chlorocyclopropyl Radical System

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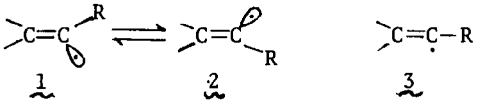
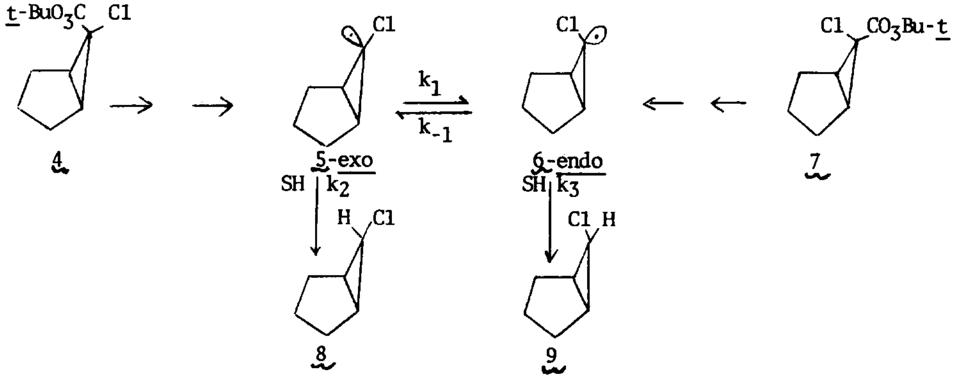
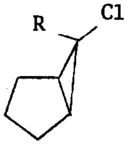
Results to date indicate that α-chloro- and α-bromovinyl radicals are bent and that scavenging by hydrogen atom transfer from hydrocarbon solvents is competitive with inversion ($1 \rightleftarrows 2$). (1) Similarly hybridized α-alkylvinyl radicals invert faster than they are intercepted by hydrocarbon scavengers (2,3) although more efficient scavenging systems do lead to partial specificity in the products. (4) In contrast, α-arylvinyl radicals appear to be linear (3, sp-hybridized) (5,6).



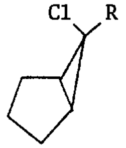
We now have extended our studies to cyclopropyl radicals with the idea that α-halocyclopropyl radicals might exhibit the same tendency towards stereospecific capture by hydrocarbon solvents as do the α-halovinyl radicals. The system we chose for our study is the 6-chlorobicyclo[3.1.0]hex-6-yl radical system ($5 \rightleftarrows 6$) which can be generated by thermolysis and photolysis of the t-butyl peroxyester precursors (4,7).



Peroxyesters 4 and 7 were prepared as follows. The readily available epimeric carboxaldehydes (10 and 11) (7) were oxidized with silver oxide to the corresponding carboxylic acids (12, m.p. 115-119°; 13, m.p. 98-103°). The latter yield the t-butyl peroxyesters by reaction with N,N-carbonyldiimidazole and sodium t-butyl hydroperoxide. (8) (7, liquid, calcd. for $C_{11}H_{17}O_3Cl$: C, 56.60, H, 7.36. Found: C, 56.89, H, 7.38. 4, m.p. 34-6°. Found: C, 56.64, H, 7.47.)



10, R=CHO
12, R=COOH



11, R=CHO
13, R=COOH

The chlorocarbon products (8,9) were prepared by addition of chlorocarbene to cyclopentene and were isolated by preparative vpc. The exo and endo isomers were identified by comparison of their nmr spectra with published data. (9) The original structural assignments are based in part on the greater thermal lability of the endo isomer in accord with the Woodward-Hoffman orbital symmetry arguments. (10)

Table 1 lists the products from the photochemical decomposition of peroxyesters 4 and 7. The thermal decomposition of the peroxyesters (106°, $k \approx 10^{-5}$ sec) does not provide reliable chlorocarbon product data because of the thermal lability of the endo-isomer (9). However, control experiments showed that both the endo and exo chlorocarbons are stable under the photochemical conditions given in Table 1. (11)

Table 1. Products from the Photodecomposition of Peroxyesters 4 and 7.[a]

Peroxyester	Scavenging System	Temp.(°C)	Products Chlorocarbons[b]	 Acid[c]	endo/exo
			—— Mole %	——	
7	Toluene	42	70 ± 5.0		0.54 ± 0.01
4	Toluene	42	64 ± 4.7		0.56 ± 0.01
7	Toluene	26	43 ± 3.0	14.6 ± 1.0	0.50 ± 0.01
4	Toluene	26	42 ± 2.0	10.7 ± 0.3	0.48 ± 0.01
7	Toluene	4	20 ± 1.0	17.0 ± 1.0	0.39 ± 0.02
4	Toluene	4	44 ± 3.0	15.2 ± 0.2	0.39 ± 0.02
7	Diisopropylbenzene	52	75 ± 4.0	15.2[d]	2.03 ± 0.04
4	Diisopropylbenzene	52	73 ± 2.0	8.3 ± 0.2	2.08 ± 0.03
7	Diisopropylbenzene	26	60 ± 1.0	14.9 ± 2.0	1.70 ± 0.01
4	Diisopropylbenzene	26	43 ± 1.0	6.8 ± 0.1	1.75 ± 0.02
7	Diisopropylbenzene	4	61 ± 1.0	18.3 ± 0.1	1.47 ± 0.03
4	Diisopropylbenzene	4	57 ± 2.0	9.6[d]	1.43 ± 0.05

[a] Degassed and sealed Quartz ampoules were irradiated with a 450-w Hanovia arc using a Corex

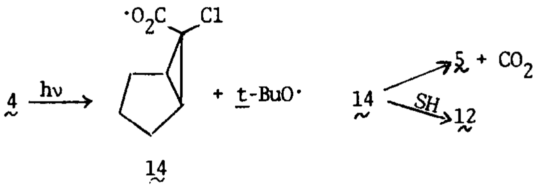
filter. Samples were 0.1 *M* in peroxyester.

[b] Vpc analysis on a 20% SE-52 on Chromsorb P column at 65° and a flow rate of 110 cc/sec. Yields determined by comparison with standard solutions of the chlorocarbons.

[c] Determined by infrared analysis using standard solutions of the acids.

[d] Single determination. All other runs represent two or more determinations.

The significant acid yields suggest that a one-bond homolysis mechanism operates with these peroxyesters (8). However, considerable decarboxylation occurs (**14** → **5**) as indicated by the generally moderate to large chlorocarbon yields.



Essentially identical *endo*/*exo* ratios are observed from either starting source. Further, with diisopropylbenzene (DIP) as scavenger, the isomer ratio is unchanged by dilution with benzene down to 1.5 *M* DIP at 26°. We conclude that the chlorocarbon products are stereoselectively determined, i.e., that equilibration (**5**⇄**6**) preceeds the hydrogen atom transfer steps. Accordingly,

$$\text{Log }(\textit{endo}/\textit{exo}) = (\Delta\Delta H^{\ddagger}_{\textit{exo-endo}} + \Delta H_{\textit{exo-endo}})/(2.3\ RT) - (\Delta\Delta S^{\ddagger}_{\textit{exo-endo}} + \Delta S_{\textit{exo-endo}})/2.3\ R.$$

Plots of the data from Table 1 as Log (*endo*/*exo*) vs T^{-1} lead to values of $(\Delta\Delta H^{\ddagger}_{\textit{exo-endo}} + \Delta H_{\textit{exo-endo}})$ for DIP and toluene of -1.22 and -1.78 kcal/mole, respectively (12).

If the *exo*-α-chlorocyclopropyl radical is more stable than the *endo*, $\Delta H_{\textit{exo-endo}}$ is negative while $\Delta\Delta H^{\ddagger}_{\textit{exo-endo}}$ is expected to be positive (13). The overall negative slopes result from a domination by the enthalpy of formation term. Assuming that $\Delta H_{\textit{exo-endo}}$ is the same in both hydrocarbon solvents, we conclude from a comparison of the two slope values that DIP is more selective than toluene by ~0.3 kcal/mole. This value is slightly smaller than the relative stereoselectivity values for cumene and toluene obtained in previously studied vinyl radical systems (5).

The alternative scheme of a single, planar α-chlorocyclopropyl radical that partitions to both products also could lead to the observed product distribution if $\Delta\Delta H^{\ddagger}_{\text{exo-endo}} < 0$. Such a situation could arise if the steric strain resulting from the chlorine-propano bridge interaction (transition state involving *exo* approach) were greater than the steric strain resulting from the interaction between the incoming scavenger and the propano bridge (transition state involving *endo* approach). Admittedly, a kinetic argument cannot conclusively choose between the two schemes. However, by either scheme, the difference between the slope values is a measure of the relative stereoselectivity of toluene and DIP in this system so that $(\Delta\Delta\Delta H^{\ddagger}_{exo\text{-}endo})_{toluene\text{-}DIP} = 0.3$ kcal/mole.

We prefer the first scheme of interconverting epimeric radicals on the basis of the reported stereospecific reduction of epimeric *gem*-halofluorocyclopropanes with tri-*n*-butyl tin hydride (14). In this reaction, pyramidal α-fluorocyclopropyl radicals are scavenged by hydrogen atom transfer from the much more efficient hydride scavenger before inversion.

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11) Toluene and diisopropylbenzene solutions of *exo*-*endo* mixtures of the chlorocarbons in degassed and sealed Quartz ampoules were irradiated for 9 hours at 26° using a 450-w Hanovia arc through a Corex filter (cutoff ~2800A). The *endo*/*exo* ratio and the total chlorocarbon content did not change under these conditions. Variable results were observed using a Vycor filter (cutoff ~2500A). Apparently, the longer wavelength filter retards excitation to a state that appears as a shoulder in the 2500-2700 A region ($\varepsilon \simeq 10$, cyclohexane) which then directly or indirectly leads to decomposition.

12) The subscripts *exo* and *endo* refer to the stereochemistry of the chlorine substituent.

13) We would expect that in the transition state involving *endo* approach by the scavenger to radical **5** greater steric strain would result than in the transition state involving *exo* approach to radical **6** so that $\Delta\Delta H^{\ddagger}_{exo\text{-}endo} > 0$.

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