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# SMALL RING COMPOUNDS XX CYCLOPROPYL RADICALS

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The generation and chemical behaviors of cyclopropyl cations or anions have been well studied, while the nature of cyclopropyl radicals is quite ambiguous as yet. It has been thought that the generation of cyclopropyl radicals is relatively difficult as compared with other hydrocarbon radicals(1).
Present study is designed to explore the nature of cyclopropyl radicals in connection with the following three points.

(1) The configurational stability of cyclopropyl radicals.

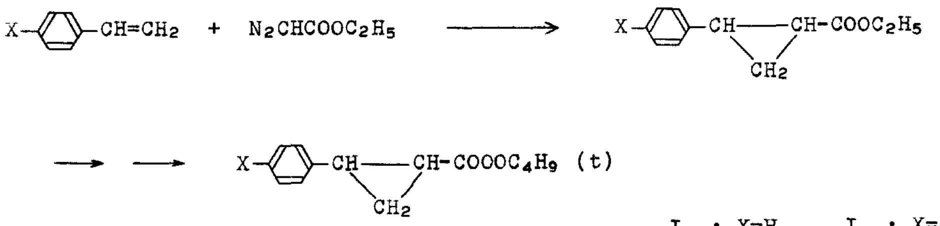
(2) The participation of cyclopropane ring in the transition state of radical generation.

(3) The relative reactivity of cyclopropyl radicals.

Generally, cyclopropyl anions are configurationally stable, whereas cations usually give rearranged products through concerted ring opening. The convincing evidence would be still insufficient for establishing the planar configuration of cyclopropyl radicals suggested by Applequist(2), thus the retention of configuration of the radicals might be expected under an appropriate reaction condition. Although cyclopropyl radicals have been generated under a variety of conditions(1), those reactions would not be suitable for the present purposes mentioned above.

In the present study, the syntheses (SCHEME 1) and the thermal decompositions of a series of t-butyl percyclopropanecarboxylate ($I_{a\sim d}$) were investigated.

SCHEME 1



$I_a$ ; X=H  $I_c$ ; X=Cl

$I_b$ ; X=$CH_3$  $I_d$ ; X=$NO_2$

The peresters synthesized are summarized in TABLE 1

TABLE 1

| | X | mp | yield(%) | IR(>CO, $cm^{-1}$) | C Calcd. | C Found | H Calcd. | H Found |
|---|---|---|---|---|---|---|---|---|
| $I_a$ | H (cis) | liquid | — | 1770 | | | | |
| $I_a$ | H (trans) | 75-76 | 80 | 1765 | 71.77 | 71.80 | 7.74 | 7.97 |
| $I_b$ | $CH_3$ ( " ) | 106.5-108.5 | 60 | " | 72.55 | 72.62 | 8.12 | 8.12 |
| $I_c$ | Cl ( " ) | 120-121 | 71 | " | 62.57 | 62.84 | 6.38 | 6.53 |
| $I_d$ | $NO_2$ ( " ) | 135-138 | 61 | " | 60.20 | 60.47 | 6.14 | 6.18 |

The reaction products obtained from the thermal decomposition (120°, 12 hr) of the trans isomer of $I_a$ in carbon tetrachloride were trans-2-phenylcyclopropyl chloride (II, trans) (45.6%, moles of product/moles of the perester decomposed), cis-2-phenylcyclopropyl chloride (II, cis) (1.3%), trans-2-phenylcyclopropanecarboxylic acid (2.3%), an unidentified product (1.5%) and a high-boiling tarry product. The formation of II would indicate that $I_a$ was decomposed homolytically and the resulting cyclopropyl radical abstracted chlorine from the solvent. The trans/cis ratio of II is 36, while the trans/cis ratio obtained from the thermal decomposition of the cis isomer of $I_a$ is 16.5. Thus, the decompositions of both isomers of $I_a$ gave the trans isomer almost exclusively, although the trans/cis ratios are slightly different. The steric effect of the 2-phenyl group may contribute to some extent to the exclusive formation of the trans isomer. The thermodynamic rearrangement of the cis isomer of II to the trans one was not observed under the same reaction condition. That the configuration of cyclopropyl radicals is not retained has been observed also in the Hunsdieker reaction of 2-methylcyclopropanecarboxylic acid(2). Consequently, at present, it can not be concluded whether cyclopropyl radicals are pyramidal or planar. However, the relatively high stereoselectivity of 9-decalyl radical under some reaction condition(3) might suggest that the retention of configuration of cyclopropyl radicals could be achieved by finding suitable radical source and reaction condition.

The decomposition rates of $I_{a\sim d}$ in chlorobenzene were measured by the method of infra-red absorption spectra and the first-order kinetic results are summarized in TABLE 2.

TABLE 2

| X | temp | $k\times10^{-5}$ $sec^{-1}$ | $\Delta H^{\ddagger}$ kcal/mol | $\Delta S^{\ddagger}_{e.u.}$(110.5°) |
|---|---|---|---|---|
| H | 101.5 | 2.60 | | |
| " | 111.5 | 9.25 | 32.5 | 6.9 |
| " | 121.5 | 25.0 | | |
| $CH_3$ | 110.5 | 9.25 | | |
| Cl | " | 7.39 | | |
| $NO_2$ | " | 5.79 | | |

The kinetic results indicate the decomposition of $I_a$ is faster than t-butyl perbenzoate and slower than t-butyl perisobutyrate. The activation parameters obtained for $I_a$ would be reasonable value for the non-concerted decomposition of a perester. Furthermore, the plot of the decomposition rates of $I_{a\sim d}$ against Hammett $\sigma$ gave a linear relationship with a slop of -0.20 ($\rho$ value) at 110.5° and the negative value of $\rho$ may exclude the Criegee type decomposition of the peresters. In comparison with the $\rho$-value(4) (-0.59 at 100°) obtained for the decompositions of p-substituted t-butyl perbenzoates and in view of the extent of the transmission of the substituent effect by cyclopropane ring, the $\rho$ value of -0.20 would be quite reasonable for non-concerted decompositions of $I_{a\sim d}$. Consequently, the decompositions of $I_{a\sim d}$ are non-concerted in nature and the cyclopropane ring does not contribute to the decomposition in any non-classical sense. The relative reactivity of a radical to some hydrogen donors can be determined by carring out the following competing reaction.

$$R\cdot \quad + \quad CCl_4 \xrightarrow{k_1} RCl \quad + \quad \cdot CCl_3$$

$$R\cdot \quad + \quad R'H \xrightarrow{k_2} RH \quad + \quad \cdot R'$$

$$k_2/k_1 = \frac{[RH]}{[RCl]} \cdot \frac{[CCl_4]}{[R'H]}$$

The values of $k_2/k_1$ obtained for the cyclopropyl radical generated from $I_a$ are summarized in TABLE 3 with the values obtained for phenyl and methyl radicals.(5)

TABLE 3

| Hydrogen donor | $C_6H_5\text{-}\triangle\cdot$ | $C_6H_5\cdot$ | $CH_3\cdot$ |
|---|---|---|---|
| Methyl Acetate | 0.028 | 0.09 | 21 |
| Acetone | 0.089 | 0.17 | 0.40 |
| Toluene | 0.104 | 0.27 | 0.75 |
| Ethylbenzene | 1.84 | 0.84 | 2.05[a] |
| Chloroform | 1.88 | 3.2 | 11.1 |
| Cyclohexane | 3.63 | 1.08 | 4.8 |

a Estimated from the date reported in reference (6).

The relative reactivity of the cyclopropyl radical seems similar to that of phenyl radical but more selective than phenyl radical, although the essence of the selectivity is uncertain as yet. Further studies on cyclopropyl radicals are in progress and the results will be reported shortly.

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