

N_a -formyl-2,16-dihydro-11-methoxytabersonine (270 mg, 97%), crystallized from chloroform-methanol: mp 180 °C dec; $[\alpha]_D -28.6^\circ$ ($c = 1.05$); ir no N-H absorption, 1745, 1680 cm^{-1} ; uv 252, 300 nm; $^1\text{H NMR}$ (60 MHz) δ 6.96 (d, 1 H, $J_{9,10} = 8$ Hz, C(9)-H), 6.66 (s, 1.5 H, C(12)-H and a masked part of C(10)-H), 6.50 (d, part of dd, 0.5 H, $J_{10,12} = 2$ and $J_{9,10} = 8$ Hz, part of C(10)-H), 5.83 (dd, 1 H, $J_{14,15} = 10$ and $J_{3,14} = 4.8$ Hz, C(14)-H), 5.20 (d, 1 H, $J_{14,15} = 10$ Hz, C(15)-H), 3.80 and 3.70 (s 3 H, C(11)-OCH₃ and C(16)-CO₂CH₃), 0.76 (t, 3 H, $J_{18,19} \sim 6$ Hz C(18)-H); MS m/e 396 (M^+), 368, 366, 310, 202, 135 (100%), 122, 121.

Coupling of Catharanthine N -Oxide (7) with N_a -formyl-2,16-dihydro-11-methoxytabersonine 2e. Trifluoroacetic anhydride (0.110 ml, 0.78 mmol) was added to a stirred solution of catharanthine N -oxide (7) (100 mg, 0.29 mmol) and N_a -formyl-2,16-dihydro-11-methoxytabersonine (2e) (117 mg, 0.3 mmol) in 0.82 ml of CH_2Cl_2 at -78°C under argon. After 50 min, the mixture was treated in usual way and the residue obtained was purified by alkaline preparative TLC (eluent CHCl_3 -MeOH (95:5), yielding 2e (110 mg, 94%) and unidentified products (37 mg).

Acknowledgment. We thank the Ligue Nationale Française contre le Cancer for a grant to F. Gueritte, Dr. P. Bladon for high resolution mass spectrometry, Dr. S. K. Kan and his co-workers and R. Z. Andriamialisoa for 240-MHz $^1\text{H NMR}$ spectrometry, and Eli Lilly Laboratories (Dr. N. Neuss) for comparison samples.

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- The numbering¹⁸ of allocatharanthine series is given between brackets (Scheme I).

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 27. Isomerization of Cyclopropylcarbinyl to Allylcarbinyl¹

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Abstract. The rate constant for isomerization of cyclopropylcarbinyl to allylcarbinyl has been measured by EPR spectroscopy. It can be represented by: $\log(k_i/s^{-1}) = (12.48 \pm 0.85) - (5.94 \pm 0.57)/\theta$, where $\theta = 2.3RT$ kcal/mol. This reaction is compared with other primary alkyl radical isomerizations.

The rapid isomerization of the cyclopropylcarbinyl radical (1) to the allylcarbinyl radical (2) is well known in free-radical chemistry.³ The rate of this reaction has not been measured

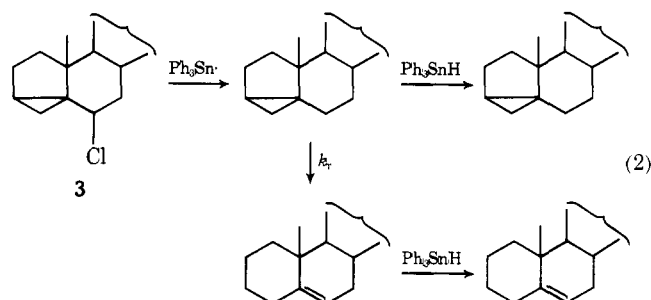
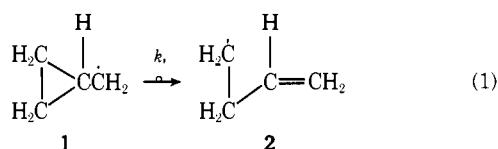
and we are aware of only one analogous reaction for which a rate constant has been estimated. For Cristol and Barbour's⁴ data on the reduction of 6 β -chloro-3 α ,5 α -cyclocholestane (3)

Table I. Isomerization of 1 to 2 in Methylcyclopropane

$T, ^\circ\text{C}$	$[1] \times 10^7, \text{M}$	$[2] \times 10^7, \text{M}$	$k_i/2k_t \times 10^7, \text{M}$
-120	0.27	2.11	18.6
-127	0.48	1.89	9.33
-128. ₆	0.49	1.43	5.60
-130. ₃	0.71	1.30	3.68
-131. ₅	0.30	1.67	11.0
-134	0.74	1.18	3.06
-135	1.43	1.20	2.21
-136	0.48	1.57	6.70
-137. ₅	1.01	1.10	2.30
-140	0.57	1.04	2.94
-141. ₃	1.20	1.60	3.73
-142	1.87	0.90	1.33
-144	2.24	1.17	1.78
-145. ₃	2.24	0.88	1.23

Table II. Bimolecular Rate Constant for Decay of 2 in Methylcyclopropane

$T, ^\circ\text{C}$	$2k_t \times 10^{-9}, \text{M}^{-1} \text{s}^{-1}$
-83	2.04
-91. ₅	1.52
-101. ₈	1.12
-111	0.83 ₅
-120	0.45



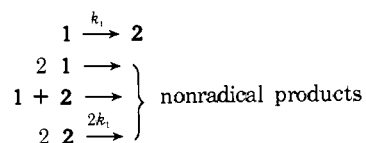
with triphenyltin hydride (eq 2), Carlsson and Ingold⁵ estimated rate constants k_r of $1.25 \times 10^8 \text{ s}^{-1}$ at 30°C , $2\text{--}5 \times 10^7 \text{ s}^{-1}$ at 15°C , $1.2 \times 10^7 \text{ s}^{-1}$ at -15°C , and $1.8 \times 10^6 \text{ s}^{-1}$ at

-20°C . The undoubted rapidity of reaction 1 makes it a valuable probe for fast reactions involving alkyl radicals. The usefulness of this reaction will obviously be improved if k_i is known, particularly if k_i is known over a range of temperatures.

Kochi, Krusic, and Eaton⁶ have shown that when cyclopropylcarbinyl is generated directly in the cavity of an EPR spectrometer, a clean spectrum due to this radical is obtained at temperatures below -140°C . Between -140 and -100°C both **1** and **2** are observed and above -100°C only **2** can be detected. This type of behavior has been exploited on several occasions in the past to obtain rate constants for similar irreversible radical isomerizations by EPR spectroscopy.⁷⁻¹¹ Provided the overall reaction scheme can be represented as shown below, then, for radicals as similar as **1** and **2**, the usual steady-state treatment yields^{10,11}

$$k_i/2k_t = ([2]^2/[1]) + [2]$$

The rate constant for the isomerization can therefore be determined by measuring the concentrations of radicals **1** and



2 under steady-state conditions and the rate constant $2k_t$ for the bimolecular self-reactions of radical **2**.

Experimental Section

The steady-state and kinetic EPR techniques required in studies of radical isomerization have been described previously.⁹⁻¹¹

Only relatively weak EPR signals due to cyclopropylcarbinyl could be obtained at -140°C by the usual photolytic procedures, e.g., photolysis of methylcyclopropane with di-*tert*-butyl peroxide or bis-trifluoromethyl peroxide, or photolysis of cyclopropylmethyl chloride with hexamethylditin or trimethylsilane (or trichlorosilane) and di-*tert*-butyl peroxide. Kochi and co-workers have generated the radical both by photolysis of the corresponding acyl peroxide^{6,12} and by photolysis of *tert*-butyl cyclopropylperacetate.¹³ We chose to use the latter compound for reasons of improved solubility and probably lower sensitivity to radical induced decomposition. The peracetate, which is fairly readily prepared,¹³ was photolyzed in methylcyclopropane as solvent.

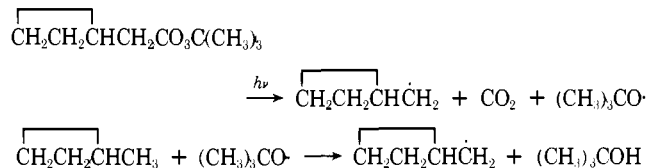


Table III. Arrhenius Parameters and Rate Constants for Isomerization of Primary Alkyl Radicals

Reaction	$\log (A/\text{s}^{-1})$	$E, \text{kcal/mol}$	k at $25^\circ\text{C}, \text{s}^{-1}$	Ref
$ \begin{array}{ccc} \begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C} \text{---} \text{C} \text{---} \text{CH}_2 \\ \\ \text{H}_2\text{C} \end{array} & \longrightarrow & \begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C} \text{---} \text{C} = \text{CH}_2 \\ \\ \text{H}_2\text{C} \end{array} \end{array} $	12.48	5.94	1.3×10^8	This work
$ \begin{array}{ccc} \text{Cyclopentyl} & \longrightarrow & \text{Cyclopentyl} \end{array} $	10.7	7.8	1.0×10^5	10
$ \begin{array}{ccc} \text{Naphthyl-CH}_2\text{CH}_2 & \longrightarrow & \text{Naphthyl-CH}_2\text{CH}_2 \end{array} $	11.75	11.3	2.9×10^3	11
$ \begin{array}{ccc} \text{Naphthyl-N(CH}_2\text{CH}_2)_2 & \longrightarrow & \text{Naphthyl-N(CH}_2\text{CH}_2)_2 \end{array} $	11.8	11.8	1.4×10^3	11
$ \begin{array}{ccc} \text{Naphthyl-N(CH}_2\text{CH}_2)_2 & \longrightarrow & \text{Naphthyl-N(CH}_2\text{CH}_2)_2 \end{array} $	11.7	12.0	8.0×10^2	11
$ \begin{array}{ccc} \text{Phenyl-CH}_2\text{CH}_2 & \longrightarrow & \text{Phenyl-CH}_2\text{CH}_2 \end{array} $	11.75	13.6	59	11

There was no sign of any induced decomposition at the temperature of our experiments and the concentration of **1** and **2** under steady illumination had the required dependence on the light intensity.⁷⁻¹¹

Results and Discussion

The data used to derive $k_i/2k_t$ are listed in Table I. These results come from three separate experiments, in each of which the temperature was changed in a random manner. A least-squares treatment of these data gives the Arrhenius equation

$$\log(k_i/2k_t/M) = (0.57 \pm 0.71) - (3.69 \pm 0.45)/\theta$$

where the errors are standard deviations and θ is $2.3RT$ kcal/mol.

The data used to derive $2k_t$ are listed in Table II. Radical **2** was generated by photolysis of *tert*-butyl cyclopropylperacetate in methylcyclopropane at temperatures where only **2** was present in detectable concentrations. Least-squares treatment of these data gives

$$\log(2k_t/M^{-1} s^{-1}) = (11.91 \pm 0.15) - (2.25 \pm 0.12)/\theta$$

Since the solvent and reactant are identical in the two sets of experiments the Arrhenius equations can be combined. This gives

$$\log(k_i/s^{-1}) = (12.48 \pm 0.85) - (5.94 \pm 0.57)/\theta$$

which yields

$$k_i = 1.3 \times 10^8 M^{-1} s^{-1} \text{ at } 25^\circ C$$

in satisfactory agreement with our earlier estimates.⁵ The pre-exponential factor is within the expected range,¹⁴ though a value closer to $10^{13.0} s^{-1}$ seems more likely to be correct,¹⁵

in which case the rate constant for isomerization at room temperature would be about $2 \times 10^8 M^{-1} s^{-1}$.

The present results and our earlier data on the isomerization of other primary, nonstabilized,^{16,17} alkyl radicals are collected, for convenience, into Table III. The wide range in the rates of isomerization of the radicals in this table illustrate both the utility and the versatility of our EPR spectroscopic techniques. We hope that our data on these isomerizations will provide useful standards for future kinetic investigations.

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3-Tricyclo[3.2.1.0^{2,7}]octyl (3-Homonortricyclyl) Cations. Steric Criteria in Degenerate Cyclopropylcarbinyl Rearrangements and the Classical vs. Nonclassical Nature of Cyclopropylcarbinyl Cations¹

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Abstract: The 3-tricyclo[3.2.1.0^{2,7}]octyl (3-homonortricyclyl) cations (**5-H**, -CH₃ and -Br) generated from different precursors under stable ion conditions underwent degenerate cyclopropylcarbinyl rearrangement, shown by their temperature-dependent proton and carbon-13 NMR spectra studied between -85 and 20 °C. The tertiary 3-chloro-3-tricyclo[3.2.1.0^{2,7}]octyl cation **5-Cl** was shown to be static and did not undergo cyclopropylcarbinyl rearrangement. Ion **5-H** was unexpectedly also formed from the allylic 2-bicyclo[3.2.1]oct-3-enyl cation (**12**). The mechanism of rearrangement of **12** into **5-H** is discussed. Based on both carbon-13 and proton chemical shifts and one-bond coupling constants (J_{C-H}) in a series of cyclopropylcarbinyl type cations, the classical vs. nonclassical nature of cyclopropylcarbinyl cations (**1**) is discussed.

The structure of cyclopropylcarbinyl cations has received much attention² and has also been subjected to theoretical treatments.³ While all experimental evidence supports the static carbenium ion nature of long lived secondary and tertiary cyclopropylcarbinyl cations^{4,5} (with varying degrees of charge

delocalization into the cyclopropyl ring), the parent, primary cyclopropylcarbinyl cation undergoes rapid degenerate rearrangement. The facile degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement taking place in the parent primary ion **1** ($R_1 = R_2 = H$) is absent when replacing hy-