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Stereochemistry of the Thermal Isomerization of *trans*-1-Ethenyl-2-methylcyclopropane to 4-Methylcyclopentene

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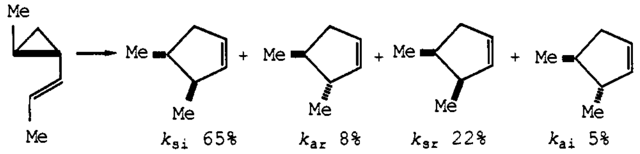
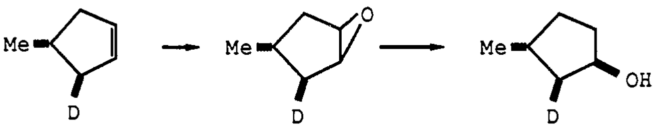
The relative importance of all four stereochemically distinct paths for thermal isomerization of *trans,trans*-1-propenyl-2-methylcyclopropane to 3,4-dimethylcyclopentenes at 296.5 °C was defined experimentally in 1976.[1]



Many new instances of the vinylcyclopropane rearrangement[2] and recent stereochemical studies with unconstrained systems[3,4] have refreshed interest in mechanistic issues. Stereochemical information has typically been hard to secure, since thermal stereomutations of substrates are faster than [1,3] sigmatropic carbon migrations in simple vinylcyclopropanes.[5] Here we report a second complete stereochemical study for a vinylcyclopropane-to-cyclopentene isomerization, based on chiral, deuterium-labeled versions of *trans*-1-ethenyl-2-methylcyclopropane.

trans-2-Methylcyclopropanecarboxylic acid was resolved by way of the (−)-(*R*)-2-phenylglycinol-derived amides,[6] HPLC separation on a Nucleosil column, and hydrolysis. The (+)-*S,S* isomer ($[\alpha]_D$ +88.0° (95% EtOH),[1,7] from 95% de amide) was converted to the corresponding 1-ethynyl-2-methylcyclopropane ($LiAlH_4$; PCC; PPh_3, CBr_4, Zn;[8] BuLi in pentane;[8] H_2O), which upon regio- and stereospecific reduction with DIBAL in CH_2Cl_2,[9] followed by D_2O, gave (+)-(1*S*,2*S*)-**1**-*E* ($[\alpha]_D$ + 91.9° ($CDCl_3$); $[\alpha]_{365}$ +299°). That the deuterium label was positioned at C2′ alone with *E* stereochemistry exclusively was confirmed through ^1H and ^2H NMR spectroscopy. Similarly, (−)-(1*R*,2*R*)-2-methylcyclopropanecarboxylic acid ($[\alpha]_D$ −90.6°; from 97% de amide) led to (1*R*,2*R*)-1-(deuterioethynyl)-2-methylcyclopropane and, in turn, to (−)-(1*R*,2*R*)-**1**-*Z* ($[\alpha]_D$ −92.6°; $[\alpha]_{365}$ −308°).

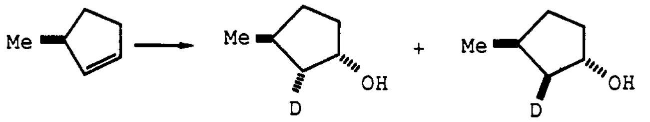
Gas-phase thermal reactions of these vinylcyclopropanes at 284.6 °C and 196–290 Torr were followed by GC; the rate constant for structural isomerizations[10] to cyclopentenes and to 1,4(*Z*)-hexadiene-6-*d* was $k_i = 4.78 \times 10^{-5}\ s^{-1}$. Recovered vinylcyclopropane **1** was assayed polarimetrically to follow racemization: $k_\alpha = 2k[(+)\text{-}\mathbf{1} \text{ to } (-)\text{-}\mathbf{1}] = 4.1 \times 10^{-5}\ s^{-1}$. The four 4-methylcyclopentenes **2** from each of four kinetic runs [two from (+)-(1*S*,2*S*)-**1**-*E* and two from (−)-(1*R*,2*R*)-**1**-*Z*] were reacted with *m*-ClPBA in $CHCl_3$ to give mixtures of epoxides with the trans isomers **3** predominating.[3,11] Analyses of these mixtures by ^2H NMR with broad-band proton decoupling gave directly the relative importance of "allowed" (si + ar) versus "forbidden" (sr + ai) products: deuterium trans to methyl, and cis to oxygen in the trans epoxide, as in (3*S*,4*R*)-**3**, came well downfield (δ 2.28) of deuterium cis to methyl, and trans to the epoxide oxygen (δ 1.33). When these samples were analyzed further in the presence of small aliquots of $Eu(hfc)_3$, the downfield, cis-to-oxygen deuterium was split into two base-line-resolved singlets, the downfield component being the more intense in product mixtures from either (1*S*,2*S*)-**1**-*E* or (1*R*,2*R*)-**1**-*Z*.



(3*S*, 4*R*)-**2** (3*S*, 4*R*)-**3** (1*R*, 2*S*, 3*R*)-**4**

Determinations of absolute stereochemistry for the trans epoxides from the cyclopentenes from (1*S*,2*S*)-**1**-*E* were secured by reducing the mixture with $LiAlH_4$ to give the corresponding 2-deuterio-3-methylcyclopentanols (^2H NMR δ 1.77, 1.33 ppm) and, in equal proportions, 3-methyl-4-deuteriocyclopentanols. Upon addition of $Eu(hfc)_3$, the deuterium NMR absorption at 1.77 ppm shifted rapidly downfield and was resolved into two components, the *downfield* one being the more intense.

(−)-(3*S*)-Cyclopentene-3-carboxylic acid[12] was reduced ($LiAlH_4$; TsCl; $LiAlH_4$) to (−)-3(*S*)-methylcyclopentene, (3*S*)-**5** [$[\alpha]_D$ −68.2° ($CDCl_3$), 43% ee],[13] which was converted largely to (1*S*,2*R*,3*S*)-**4** and (1*S*,2*S*,3*S*)-**4** [$Hg(OAc)_2$;[14] NaOD, $NaBD_4$; Ac_2O, Py; GC separation of regioisomeric acetates; $LiAlH_4$]. The ^2H NMR absorptions for this mixture, with dominant singlets at δ 1.77 and 1.33 ppm, shifted downfield and were each resolved into two components in the presence of $Eu(hfc)_3$, the *upfield* ^2H NMR component of each being the more intense. Thus there is more (3*S*,4*R*)-**3** than (3*R*,4*S*)-**3** in the trans epoxide mixture from **2** derived from either (1*S*,2*S*)-**1**-*E* or (1*R*,2*R*)-**1**-*Z*, and the vinylcyclopropane rearrangement of 1-ethenyl-2-methylcyclopropane occurs with $k_{si} > k_{ar}$ and $k_{sr} > k_{ai}$.



(3*S*)-**5** (1*S*, 2*R*, 3*S*)-**4** (1*S*, 2*S*, 3*S*)-**4**

From the experimental values of k_i, k_α, and ee for the substrates (1*S*,2*S*)-**1**-*E* or (1*R*,2*R*)-**1**-*Z* may be calculated weighted optical purities for these vinylcyclopropanes over the reaction times employed,[1] and then the observed ^2H NMR integral ratios for the epoxide mixtures derived from 3-deuterio-4-methylcyclopentene products, before and after adding $Eu(hfc)_3$, allow calculation of direct rate constants for all four components of this vinylcyclopropane-to-cyclopentene isomerization. The relative rate constants determined are summarized in the following equations; experimental uncertainties are estimated to be ±1.5%.

These stereochemical results are consistent with recent work of Gajewski and Squicciarini.[3] The close qualitative agreement

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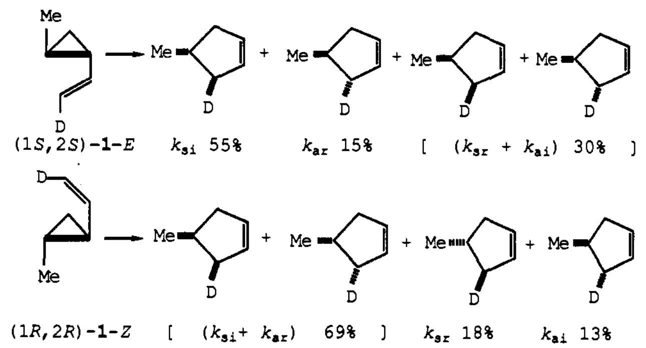

with results reported in 1976[1] for a similar vinylcyclopropane rearrangement based on totally different analytical techniques for quantifying product mixtures (GC, polarimetry) reinforces the fundamental conclusion: the direct "ai" pathway does indeed participate, and the "allowed" alternatives, while more important, are only negligibly advantaged energetically. With no significant energetic preference for concert in evidence, orbital symmetry control of stereochemistry does not seem a serviceable mechanistic rationale. The four stereochemically distinct paths used may involve four distinct diradical transition structures of closely similar energies.

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Electron Spin Resonance Study of the Radical Reactivity of C_{60}[†]

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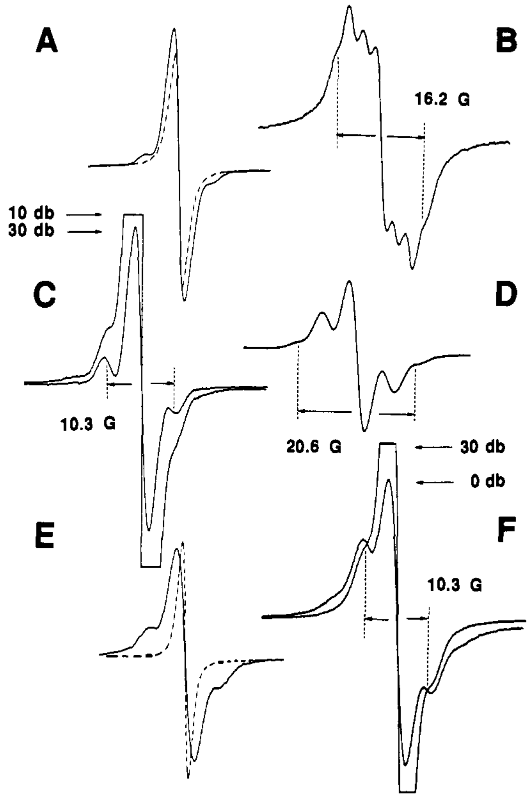

Figure 1. (A) ESR spectra at 220 K (dashed line) and 100 K (solid line) (10 dB) obtained by photolysis of a ca. 0.002 M toluene solution of C_{60} in the presence of di-*tert*-butyl peroxide. (B) ESR spectrum at 220 K obtained as in Figure 1A with [α-^{13}C]toluene as solvent. (C) The spectrum of Figure 1A (100 K) at two microwave power levels (0 dB: ca. 200 mW). (D) The spectrum of Figure 1A at 4.2 K (30 dB). (E) Spectra at 280 K (dashed line) and 100 K (solid line) (25 dB) obtained as in Figure 1A with benzene as solvent. (F) Spectrum of Figure 1E (100 K) at two microwave power levels. All spectra have the same horizontal scale.

The discovery that the novel allotropes of carbon, C_{60} and C_{70}, can be produced in chemically significant quantities with relative ease has triggered an intense interest in exploring their chemical reactivity.[1] The esthetic soccerball structure of the C_{60} framework has been confirmed by recent X-ray studies.[2] In a platinum complex, C_{60} behaves as an olefin, affording a classical transition-metal π-olefin complex.[2b] We now report our ESR results, which show (a) that a variety of photochemically generated, reactive, neutral radicals efficiently add to C_{60} to yield remarkably persistent radical adducts and (b) that the photolysis of C_{60} in the presence of donor molecules produces the radical anion of C_{60}. The latter was also generated electrochemically. The integrity of the C_{60} framework in these radical reactions is supported by the reversibility of radical addition in the case of phenylthiyl radicals and by MS analyses of the products. Spectra of frozen solutions of C_{60} radical adducts show the presence of electronic triplet species whose origin is discussed.

Brief UV photolysis in the ESR cavity of a purple toluene solution of C_{60} containing di-*tert*-butyl peroxide[3] produces an intense ESR absorption (Figure 1A) with $g = 2.00232$ and $\Delta H = 1.9$ G that does not saturate at the available microwave powers. The absorption grows in intensity as the irradiation continues and decays slowly on shuttering the light at higher temperatures. No ^{13}C satellites could be detected. After photolysis, the clear solution has a light amber color characteristic of all radical adducts of this study. Photolysis of the same solution without C_{60} produces the highly transient spectrum of the benzyl radical.[4] We conclude that $C_6H_5CH_2^{\bullet}$ radicals, produced by H atom abstraction from toluene by photochemically generated t-BuO$^{\bullet}$ radicals, readily add to C_{60}. Accordingly, the spectrum obtained in exactly the same manner using 99% [α-^{13}C]toluene clearly shows the effects of the ^{13}C label (Figure 1B). The observation of a spectrum other than the expected doublet appropriate for a hyperfine interaction with one ^{13}C ($I = {}^1/_2$) indicates that *multiple* addition of benzyl radicals took place.

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[3] (a) To a 0.003 M C_{60} toluene solution in a quartz ESR tube was added ca. $^1/_{10}$ volume of di-*tert*-butyl peroxide. (b) The UV light source was a 500-W Cermax xenon illuminator whose output passed through a circulating Kasha solution (240 g/L $NiSO_4 \cdot 6H_2O$ and 45 g/L $CoSO_4 \cdot 7H_2O$). The ESR spectrometer was a Bruker ESP 300 equipped with tracking gaussmeter and digital frequency counter.

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