Chemistry and Structure of *anti*-(*Z*)- and *syn*-(*E*)-Bis(fenchylidene)

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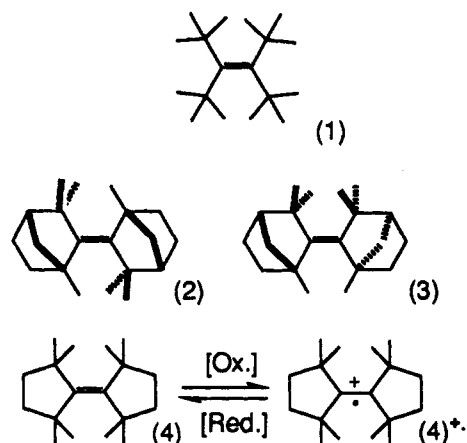*School of Chemistry, University of NSW., Kensington 2033, Australia*

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anti-(*Z*)-Bis(fenchylidene) (3) has been prepared. The crystal structure of 3 displays an alkene torsion angle of 17.0° and deformations of the carbon–carbon bond lengths and angles around the alkene center. The chemical behavior of *syn*-(*E*)-bis(fenchylidene) (2) and 3 was found to be affected by the steric strain.

We, like many other workers,[1–7] are interested in the properties of sterically hindered alkenes. The severe nonbonded interactions in such systems can lead to stretching, torsion, and rehybridization of the carbon–carbon double bond along with deformations on neighboring centers. Studies of these structural deformations have led to a better understanding of the alkene bond. In this field, the severely strained tetra-*tert*-butylethylene (1) is considered the ultimate synthetic goal.[3–20] During our attempts to synthesize 1 via "tied-back" analogues,[20] we employed the fenchane moiety as a model. Thus, bis-(fenchylidene) was prepared via the 1,3,4-Δ-selenadiazoline pyrolysis route to hindered alkenes. The syn-(*E*) isomer 2 has previously been prepared by this route in 24% yield.[3,21] The analogous 1,3,4-Δ-thiadiazoline route is reported to yield a mixture of the syn-(*E*)-2 and anti-(*Z*)-3 isomers in 72% yield, however, 3 was not isolated.[3]

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Previously, only the less strained 2 was isolated and characterized.[3] The steric strain is evident in the X-ray crystal structure of 2 which displays a double bond torsion of 11.8° and antisymmetrical out of plane deformation on the sp² carbons.[22] In comparison, force field calculations upon 3 suggested only a 1.3° torsion of the double bond.[23]

We believed that an experimental comparison of the deformation modes and spectral properties of 2 and 3 would yield further insight into strained alkene bonds. On the basis of previous work,[3,21] the pyrolysis of fenchone (triphenylphosphoranylidene)hydrazone with either selenium or fenchane selone was expected to yield only the isomer 2. Instead, we obtained up to 45% yield of 2 and 3 in a 55:45 ratio. Some of the alkene 2 was readily recovered by recrystallization from CH₃CN/Et₂O while 3 cocrystallized with more of 2 as multiple platelets. The two alkenes were also inseparable by standard TLC and column chromatographic techniques. These initial difficulties in obtaining 3 free of 2 may explain its previous anonymity. The alkene 3 was eventually isolated via chromatography on 15% w/w silver nitrate impregnated silica and analyzed by GLC (SE-52, 210 °C, or OV-1, 170 °C).

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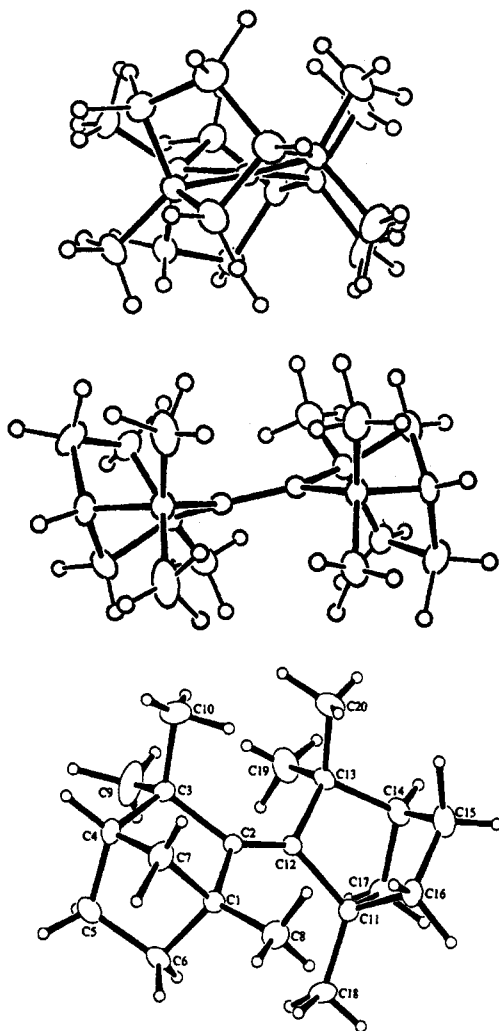(23) Favini, G.; Simonetta, M.; Sottocornola, M.; Todeschini, R. *J. Comput. Chem.* **1982**, *3*, 178.

Figure 1. Crystal structure of **3**.

Table 1. Notable Found and Calculated Structural Features for 3

structural feature	found[24]	calcd[23]
db torsion	17.0°	1.3°
db length	1.341(6) Å	1.359 Å
mean $C(sp^2)-C(sp^3)$	1.561 Å	1.543 Å
mean $C(sp^2)-C(sp^3)-C(Me)$	115.9°	
C(1)-C(2)-C(12)	126.7(4)°	128.3°
C(3)-C(2)-C(12)	129.2(4)°	128.3°
1,6-methyl contacts		
C(8)-C(18)	3.266 Å	3.014 Å
C(9)-C(19)	3.272 Å	3.216 Å
C(10)-C(20)	3.232 Å	3.234 Å

Alkene **3** formed large rectangular platelets from CH₃-CN/Et₂O. The X-ray crystal determination of **3**[24] is displayed in three projections in Figure 1.

Table 1 contains the notable structural features of **3**[24] and a comparison with calculated values.[23] Notably, the C(1)-C(2)-C(12)-C(11) torsion angle in **3** of 17.0° is greater than the comparable angle of 11.8° found in **2**[22] and is also greater than the predicted angle. The intramolecular strain is not reflected in the magnitude of the alkene bond distances of 1.341(6) and 1.349(4) Å for **3** and **2**, respectively. A more significant elongation is observed in the $C(sp^2)-C(sp^3)$ bonds, the mean being 1.561 Å. Further evidence of methyl compression is seen in the $C(sp^2)-$

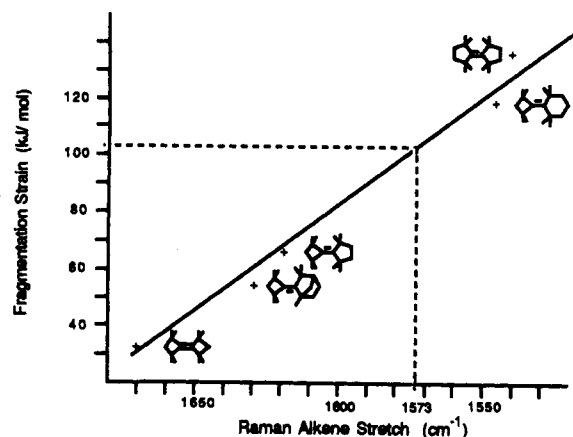(24) Brooks, P. R.; Bishop, R.; Counter, J. A.; Tiekink, E. R. T. *Z. Krist.*, in press.

Figure 2. Alkene fragmentation strain vs raman stretch.

$C(sp^3)-C(methyl)$ angles which range from 114° to 120°. Similar effects were observed for **2**.[22]

For the *syn-(E)* isomer, the small double bond torsion allows for a minimization of steric strain via the "cog-wheeling" of opposing methyl groups. The view along the alkene bond clearly shows that this is not occurring in **3**. Three pairs of close 1,6-intramolecular methyl contacts are observed. The direction of alkene torsion would suggest that the driving force is the reduction of steric compression between the two lone methyls. The congestion of the methyl groups results in a marked downfield shift in the ¹H NMR spectrum. The methyl resonances of **2** and **3** appear at δ 1.51, 1.32, 1.23 and 1.40, 1.33, 1.17 ppm, respectively. Similiar deshielding affects have previously been observed for other congested systems.[25]

The total strain energy in **2**, calculated by Allinger's MM1 field, is 254–6 kJ/mol[26,27] while the fragmentation strain was calculated to be 91.6 kJ/mol.[27] Similar calculations employing the force field of Schleyer–Androse–Mislow afforded strain energies of 266 kJ/mol for **2** and 278 kJ/mol for **3**.[28] The former calculations provided a better fit of structural parameters for **2**, while a greater strain in **3** is consistent with our thermal equilibrium results.

Krebs has found a fair correlation of fragmentation strains with the Raman alkene stretch.[29] This is not surprising as the alkene stretching frequency is indicative of the double bond force constant. Both alkenes display the same low Raman stretching frequency of 1573 cm⁻¹ in the solid state. This indicates considerable alkene strain when compared with 1675 cm⁻¹ for 2,3-dimethylbut-2-ene.[30]

The fragmentation strains versus Raman alkene stretching frequencies obtained by Krebs for strained hydrocarbon alkenes is plotted in Figure 2. The comparison for **2** and **3** yields an approximate fragmentation strain of 103 kJ/mol for both alkenes. These results, based on a calibration curve, are thought to be more reliable than the original calculation of 91.6 kJ/mol for **2**.[27]

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The two alkenes afforded identical mass spectra under 70 eV electron impact. This can only be due to both alkenes possessing a common parent ion. This suggests that rotation of alkene bond is readily occurring prior to fragmentation. Cyclic voltammetry studies have previously shown that a π electron is most readily lost from hindered alkenes, forming the radical cation.[29,31,32] The radical cations then have a far lower potential barrier to rotation than the parent alkene. It is even suggested that the cyclopentyl groups of $4^{.+}$ are orthogonal.[32] The identical mass spectra strongly support the interconversion process shown in Scheme 1.

This isomerization is also observed in dichloromethane catalyzed by aluminum chloride. A 52:48 equilibrium ratio is obtained via the radical cations within 30 min. A further slow decomposition also occurs.

The alkenes thermally isomerize at 250 °C. The individual alkenes, sealed in capillary tubes, were heated for varying lengths of time and analyzed by GLC. An equilibrium ratio of 55:45 2/3 was obtained, giving a free energy difference of 872 J/mol at 250 °C. The alkenes were stable at this temperature with no further decomposition.
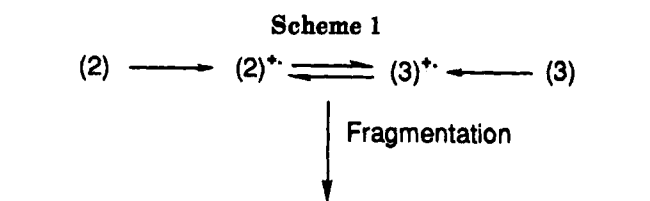
The known 2 undergoes normal alkene ozonolysis and epoxidation, affording the expected products.[3] The absence of diradical character in 2 is demonstrated by its stability toward molecular oxygen.[3] Surprisingly, the reaction of 2 with bromine has not been reported.

We have found that solutions of 2 readily decolorize bromine. These reactions rapidly form dark insoluble materials upon exposure to light, suggesting a radical mechanism is present. In the absence of light, the alkene consumes 4 equiv of bromine. These reactions, performed at ambient temperatures, or –78 °C, were complex mixtures by TLC and NMR examination. The mechanism of this complex reaction can only be speculated.

The initial formation of the bromonium ion 5 is probable, which then decomposes with rearrangement. The rearface nucleophilic attack upon 5 will be extremely hindered. When it was attempted to trap cation intermediates by repetition of the experiment at –78 °C, with one equivalence of bromine in the presence of methanol, 50% of unreacted 2 and no methoxy-containing material was observed by ^{1}H NMR. Instead, the bromomethyl derivative 6 was isolated in 15% yield.
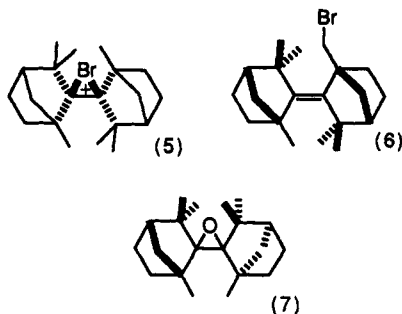
In comparison, 3 reacts only slowly with bromine. Light accelerates this reaction greatly. In either case hydrogen bromide and insoluble dark tars are formed. In the mother liquor the major component is unreacted 3, with no new

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Scheme 1

$$(2) \longrightarrow (2)^{.+} \rightleftharpoons (3)^{.+} \longleftarrow (3)$$

Fragmentation

products being isolated from the reactions. The normal electrophilic first step is thought to be occurring, followed by decomposition of the bromonium ion. The rate difference compared to 2 reflects equal steric hindrance upon both faces of the alkene.

The alkene 3 exhibited normal behavior toward m-chloroperbenzoic acid, affording the expected epoxide 7 in 27% yield, with unreacted alkene being recovered in 9% yield.

Experimental Section

Melting points were recorded on a Kofler hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi 260-10 instrument. Raman spectra were recorded using the 488.0-nm line of an argon ion laser at 40 mW. The monochromator was a Tobin Yuon U-1000 instrument, and data collection was on a Hicom AT instrument. The ^{1}H NMR spectrum of 7 was recorded on a CXP-300 at 300 MHz, all other ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-500 instrument at 500 and 126 MHz, respectively, and are recorded relative to tetramethylsilane. Optical rotations were obtained on a Perkin-Elmer 141 polarimeter. Routine mass spectra were obtained on a AEI MS-12 instrument at 70 eV. High-resolution mass spectra were recorded on a GIZMO Mark 7. The X-ray crystal structure of 3 was recorded on a Enraf-Nonius CAD 4F diffractometer controlled by a PDP8/A computer using graphite-monochromated Mo Kα radiation. (1R)-(-)-Fenchone (Aldrich Chemical Co.; 98+%) was used for all preparative work.

syn-(E)- (2) and anti-(Z)-Bis(fenchylidenes) (3). Method A. Fenchone selone (100 mg, 0.47 mmol) and fenchone (triphenylphosphoranylidene)hydrazone (200 mg, 0.47 mmol) were heated under argon for 16 h at 180 °C. The volatiles were then removed at 20 °C/0.1 mmHg. The hexane-soluble fraction of the residue was purified on an alumina column with hexane, yield of 2 and 3, 3:1, 30 mg, 23%.

Method B. Fenchone (triphenylphosphoranylidene)hydrazone (5 g) was ground together with fresh selenium (30 g, 0.375 mol). Further hydrazone derivative (35 g, total; 0.094 mol) and CH$_2$Cl$_2$ (20 mL) were added, and then the mixture was evaporated. Pyrolysis under argon at 210 °C overnight yielded, after the usual workup,[3] 2 and 3, 55:45, 11.5 g, 45%. Recrystallization from CH$_3$CN afforded 2, 5.0 g. For separating the remaining alkene mixture (1:2 2/3), a column was prepared via evaporating AgNO$_3$ (15 g) in CH$_3$CN (200 mL) onto silica gel (100 g). Elution of 1.0-g samples with hexane afforded first 3 (total 4.9 g) then 2 (total 2.9 g).

syn-(E)-2: mp 125–7 °C (lit.[3] 125–7 °C); IR ν_{max} (paraffin mull) 3040, 3020, 1365, 1203, 1150, 1110, 968, 894 cm^{-1}; Raman ν_{max} (solid state) 1573 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.90 (dq, J = 9.7 Hz and 2.0 Hz, 2H), 1.76–1.66 (comp m, 4H), 1.55–1.43 (comp m, 5H), 1.51 (s, 6H), 1.34–1.17 (comp m, 3H), 1.32 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 147.2 (C), 52.7 (CH), 51.8 (C), 49.3 (CH$_2$), 47.6 (C), 36.0 (CH$_2$), 30.7 (CH$_3$), 27.7 (CH$_3$), 27.3 (CH$_3$), 25.6 (CH$_2$); MS m/z$^+$ (70 eV) 272 (22), 257 (9), 229 (22), 216 (5), 203 (50), 191 (36), 161 (23), 147 (66), 121 (100), 107 (67); optical rotation lit.[3] $[\alpha]^{23}_D$ =–240.0° (c = 0.3 in EtOH).

anti-(Z)-3: mp 92–3 °C; IR ν_{max} (paraffin mull) 3060, 3025, 1368, 1262, 1208, 1152, 1113, 973, 884, cm^{-1}; Raman ν_{max} (solid state) 1573 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.85–1.71 (comp m, 4H), 1.58–1.48 (comp m, 4H), 1.40 (s, 6H), 1.40–1.32 (comp m, 4H), 1.33 (s, 6H), 1.17 (s, 6H), 1.15 (d, J = 9.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 148.7 (C), 53.7 (C), 51.5 (CH), 50.7 (CH$_2$), 48.6 (C), 35.4 (CH$_2$), 29.9 (CH$_3$), 29.8 (CH$_3$), 26.2 (CH$_2$), 25.8 (CH$_3$); MS m/z$^+$ (70 eV) 272 (22), 257 (9), 229 (22), 216 (5), 203 (50), 191 (36), 161 (23), 147 (66), 121 (100), 107 (67%); optical rotation; $[\alpha]^{25}_D$ =

–206° (c = 0.57 in EtOH). Anal. Calcd for C$_{20}$H$_{32}$: C, 88.16; H, 11.84. Found: C, 87.94; H, 11.72.

1′-(Bromomethyl) Derivative 6. To a suspension of 2 (100 mg, 0.37 mmol) in dry CH$_2$Cl$_2$/MeOH (4:1, 2.5 mL) at –78 °C was added bromine (20 µL, 59 mg, 0.37 mmol). The solution slowly decolorized and, after 20 min, was allowed to warm to room temperature. The solution was washed with water (2 mL) and then saturated NaHCO$_3$ (2 mL), dried, and evaporated. The ^{1}H NMR spectra at this stage displayed 50% alkene 2 and no methoxy groups. Elution through silica with hexane afforded 6, 22 mg, 15% yield, as colorless platelets: mp 59–64 °C; IR ν_{max} (paraffin mull) 1373, 1362, 1311, 1297, 1286, 1248, 1229, 1200, 1145, 1108, 966, 854 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.22 (d, J = 10.2 Hz, 1H), 3.93 (d, J = 10.2 Hz, 1H), 2.00–1.96 (comp m, 1H), 1.91 (dq, J = 9.8 and 1.8 Hz, 1H), 1.85–1.79 (comp m, 1H), 1.77–1.67 (comp m, 2H), 1.64–1.58 (comp m, 1H), 1.53–1.48 (comp m, 4H), 1.51 (s, 3H), 1.39–1.31 (comp m, 2H), 1.34 (s, 3H), 1.33 (s, 3H), 1.28–1.23 (comp m, 1H), 1.27 (s, 3H), 1.20 (s, 3H), 1.05 (dd, J = 9.85 and 1.65 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 148.7 (C), 144.1 (C), 56.1 (C), 53.1 (CH), 52.1 (C), 52.0 (CH), 49.3 (CH$_2$), 48.5 (C), 47.7 (C), 45.3 (CH$_2$), 44.3 (CH$_2$), 36.0 (CH$_2$), 32.0 (CH$_2$), 31.1 (CH$_3$), 30.2 (CH$_3$), 27.7 (CH$_3$), 27.6 (CH$_3$), 26.9 (CH$_3$), 25.8 (CH$_2$), 25.4 (CH$_2$); M$^+$ found 350.16047, calcd for C$_{20}$H$_{31}$Br 350.16091; MS m/z$^+$ (70 eV) 352 (3), 350 (3), 309 (2), 307 (2), 283 (4), 281 (5), 271 (100), 255 (11), 241 (6), 227 (15), 215 (28), 201 (22), 191 (25).

Epoxide 7. Alkene 3 (0.55 g, 2.0 mmol) was added with stirring to m-chloroperbenzoic acid (0.7 g, 4.5 mmol) in chloroform (10 mL). After 1 h, the solution was washed with sodium bicarbonate solution (10 mL), dried, and then evaporated. Elution through silica with hexane/ethyl acetate gave the epoxide 7, 0.16 g, 27%, and alkene 3, 0.05 g, 9%: mp 128–30 °C; IR (paraffin mull) 1362,

1305, 1145, 1105, 1012, 982, 973, 939, 894, 868 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.14–2.06 (m, 1H), 1.98 (d, J = 9.9 Hz, 1H), 1.87 (d, J = 9.9 Hz, 1H), 1.88–1.71 (m, 3H), 1.59–1.50 (m, 4H), 1.40–1.20 (m, 3H), 1.29 (s, 3H), 1.16 (s, 3H), 1.075 (s, 3H), 1.066 (s, 3H), 1.02 (s, 3H), 1.00–0.95 (m, 1H), 0.98 (s, 3H); M$^+$ found 288.24428, calcd for C$_{20}$H$_{32}$O 288.24458; MS m/z$^+$ (70 eV) 288 (6), 259 (19), 245 (15), 219 (60), 207 (100), 189 (39), 165 (79), 163 (57), 151 (100), 137 (100), 135 (97), 121 (100), 119 (100).

Thermal Equilibrium of 2 and 3. The individual alkenes (>99%) were sealed under vacuum in capillary tubes and then held in a Woods metal bath maintained at 250 ± 2 °C. Tubes were withdrawn at the required times and cooled quickly and then the contents analyzed by GLC (OV-101, 170 °C).

Aluminum Chloride Catalyzed Isomerization of 2 and 3. To solutions of the alkenes in dry CH$_2$Cl$_2$ (0.1 M) under N$_2$ was added anhydrous AlCl$_3$ (1 equiv). GLC analysis (OV-101) indicated rapid isomerization and equilibrium establishment in 30 min (52:48 2/3).

Supplementary Material Available: The ^{1}H NMR spectrum of 7 (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.