

# X-ray Crystal Structure of 3-Vinylcyclopropene. Gas Phase Synthesis of Simple Cyclopropenes

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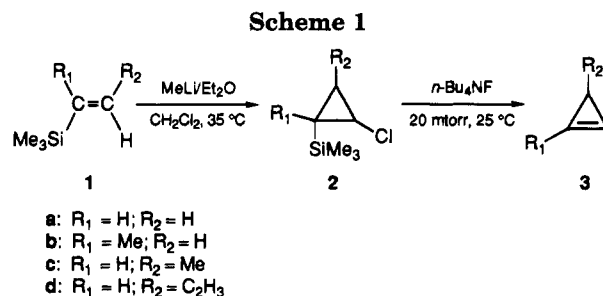
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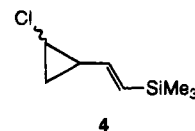
The vacuum gas-phase elimination of  $\beta$ -halocyclopropylsilanes over solid fluoride has been used to synthesize cyclopropenes for structural characterization by X-ray crystallography.

By virtue of the unusual bonding properties that result from their high energy content, the cyclopropenes represent one of the cornerstones of modern structural chemistry.<sup>1,2</sup> As part of our program on the synthesis and structure of compounds containing this ring system,<sup>3</sup> we have used the vacuum gas–solid reaction procedure described previously<sup>4–6</sup> to prepare cyclopropene and some of its derivatives for structural characterization by X-ray crystallography. The salient feature of these syntheses is the use of solid fluoride to effect the gas-phase elimination of  $\beta$ -halocyclopropylsilanes. We report these results here including the X-ray crystal structure of 3-vinylcyclopropene (**3d**).

The syntheses are presented in Scheme 1. The gas-phase route to cyclopropene<sup>7,8</sup> provides an attractive new synthesis of this hydrocarbon as well as of the derivatives **3b**<sup>9</sup> and **3c**.<sup>10</sup> The yields (65–75%) of **3a–c** were determined by isolating the cyclopropenes as the Diels–Alder adducts of cyclopentadiene.<sup>11</sup> Although derivatives of 3-vinylcyclopropene are fairly common,<sup>12</sup> the parent hydrocarbon has not been reported. The desired precur-



sor **2d** could be separated from **4** by preparative gas



chromatography. Elimination of **2d** over solid fluoride provided the desired cyclopropene **3d**.

Our original intent was to derive the structure of cyclopropene itself by X-ray crystallography using the low-temperature technique described earlier.<sup>13,14</sup> Although the in situ crystallization of cyclopropene (mp 126 K) was performed successfully at 104 K, further cooling led to a solid–solid phase transition, and the crystal was damaged. The molecule was found to be disordered or twinned on a 3-fold axis, and the carbon–carbon distances (1.414(3) Å) represent a mean value between the expected double and single bond distances. Further refinement was not possible. Efforts to carry out structural studies using either **3b** or **3c** were not undertaken.

In the case of 3-vinylcyclopropene (mp –92 °C) it was possible to secure good structural information by X-ray

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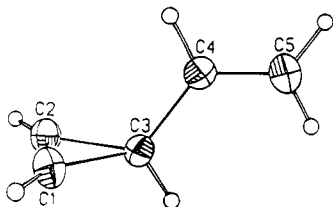
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(11) Trapping experiments using cyclopentadiene were carried out by introducing about 0.2 mL of the diene into the cold trap<sup>4</sup> used to collect the cyclopropenes. The elimination reaction was carried out, and more cyclopentadiene (1.0 mL) was then added. The mixture was allowed to melt slowly and then stirred for 3 h at –50 °C. The trap was cooled to –78 °C and the excess cyclopentadiene removed *in vacuo*. The residue was dissolved in pentane and purified by preparative gas chromatography or thin layer chromatography. The Diels–Alder adducts of **3a**, **3b**, and **3c** have been described previously in refs 7, 9, and 10, respectively.

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**Figure 1.** Molecular structure of **3d**. The ellipsoids are drawn at the 50% level.

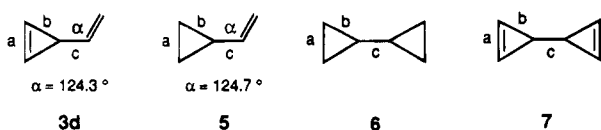
**Table 1. Interatomic Distances and Angles for 3d**

atoms	distance (Å)	atoms	angle (deg)
C(1)–C(2)	1.279(1)	C(1)–C(2)–C(3)	65.0(1)
C(1)–C(3)	1.516(1)	C(2)–C(1)–C(3)	65.1(1)
C(2)–C(3)	1.517(1)	C(1)–C(3)–C(2)	49.9(1)
C(3)–C(4)	1.476(1)	C(1)–C(3)–C(4)	121.1(1)
C(4)–C(5)	1.330(1)	C(2)–C(3)–C(4)	121.0(1)
		C(3)–C(4)–C(5)	124.3(1)

**Table 2. Bond Lengths and Angles for Selected Cyclopropanes and Cyclopropenes**

compd	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	ref
<b>3d</b>	1.279	1.516	1.476	this work
<b>7</b>	1.290	1.512	1.503	3
$\Delta$ (Å)	-0.011	+0.004	-0.027	$\sigma = 0.001$ Å
<b>5</b>	1.499	1.515	1.473	15
<b>6</b>	1.505	1.505	1.492	15
$\Delta$ (Å)	-0.006	+0.010	-0.019	$\sigma = 0.001$ Å

crystallography. To the best of our knowledge, this is the first time that the X-ray crystal structure of a simple cyclopropene has been determined. The molecular structure and bond distances and angles are presented in Figure 1 and Table 1, respectively. The structural parameters of **3d** are compared in Table 2 with those determined for the structurally related compounds **5–7**.



**Figure 2.** X-X electron density difference maps for **3d**, positive and zero contour lines are drawn at distances of  $0.05 \text{ e}\text{\AA}^{-3}$ , negative are dashed at distances of  $0.1 \text{ e}\text{\AA}^{-3}$ , the sections for the maps A–D are displayed in the perspective view of the molecule.

**Table 3. Calculated Bond Lengths and Angles for 3d**

atoms	AM1	STO-3G	3-21G*	6-31G*	6-31++G**	expt
C(1)–C(2)	1.312	1.277	1.282	1.275	1.275	1.279
C(1)–C(3)	1.491	1.499	1.527	1.500	1.502	1.516
C(3)–C(4)	1.476	1.513	1.481	1.490	1.489	1.476
C(4)–C(5)	1.329	1.310	1.318	1.320	1.322	1.330
C(1)–H(1)	1.073	1.075	1.059	1.068	1.068	
C(3)–H(2)	1.108	1.089	1.076	1.084	1.083	
C(4)–H(3)	1.096	1.085	1.076	1.080	1.080	
C(5)–H(4)	1.086	1.081	1.073	1.075	1.076	
C(5)–H(5)	1.087	1.081	1.075	1.077	1.078	
C(1)–C(2)–C(3)	63.9	64.8	65.2	64.9	64.9	65.0
C(1)–C(3)–C(2)	52.2	50.4	49.7	50.3	50.2	49.9
C(1)–C(3)–C(4)	119.7	121.5	119.7	121.4	121.2	121.1
C(3)–C(4)–C(5)	122.4	124.1	124.8	124.6	124.6	124.3

The most striking feature of the bond lengths found for **3d** is the shortening of bonds *a* and *c* and a lengthening of bond *b*. This may be attributed to the presence of  $\pi(\text{C}=\text{C})-\pi(\text{Walsh})$  conjugation, as observed earlier by Nijveldt and Vos<sup>15</sup> for vinylcyclopropane **5** (Table 2). The effect is not observed in **6** where both cyclopropyl bonds are the same length. The  $\pi(\text{C}=\text{C})-\pi(\text{Walsh})$  interaction is probably common for most vinylcyclopropanes and vinylcyclopropenes in the bisected conformation and also accounts for the short double bond in **3d** (1.279 Å) as compared to the significantly longer cyclopropenyl double bonds in **7** (1.290 Å).<sup>3</sup> A through-space interaction between the two double bonds in 3-vinylcyclopropene could not be detected from the bond lengths and angles ( $\alpha = 124.3$  in **3d** versus 124.7 in **5**) or in the X–X electron density maps (Figure 2).

Structures for 3-vinylcyclopropene calculated using a variety of methods at different levels are summarized in Table 3. Although the distortions associated with cyclopropenes are usually better described with diffused-polarized basis sets (6-31++G\*\*), replication of the

experimental results can be achieved reasonably well at a lower level of theory in this case.<sup>16</sup>

Future studies will include structure determination of other cyclopropenyl compounds.

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**Supplementary Material Available:** Experimental details and spectral data for **2a–d** and **3d** (3 pages). 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.

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