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Chlorinated Cyclopropenylidenes, Vinylidenecarbenes, and Propargylenes: Identification by Matrix Isolation Spectroscopy[†]

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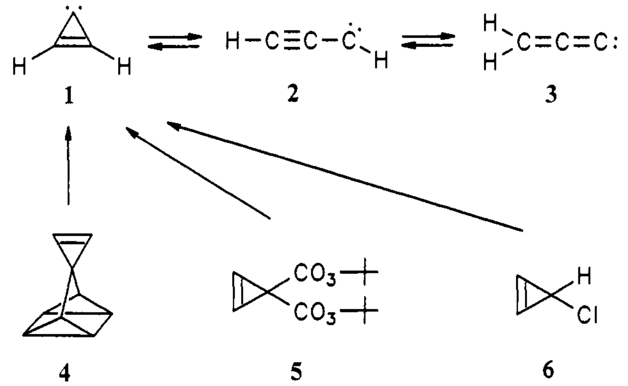
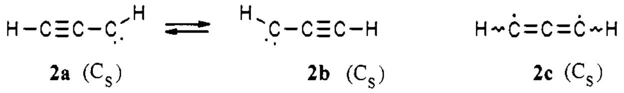
Abstract: Matrix-isolated mono- and dichlorocyclopropenylidene have been generated by high-vacuum flash pyrolysis from di- and trichlorocyclopropenes. By subsequent photolysis they have been isomerized to the corresponding vinylidenecarbenes and propargylenes. The identification of six new carbenes is based on the comparison of their experimental and calculated (MP2/6-31G*) infrared spectra. All have singlet electronic ground states.

Introduction

The isomeric C_3H_2 carbenes cyclopropenylidene (**1**), propargylene (**2**), and vinylidenecarbene (**3**) are of considerable interest for theoretical chemistry[1] as well as for chemistry in interstellar space, where at least **1**[2] and **3**[3] play an important role. Rotational lines of these two are easily detected by radioastronomy since both have singlet electronic ground states and very large dipole moments. As it was shown in 1965[4] the third isomer propargylene (**2**) is a triplet carbene. Its dipole moment is predicted to be very small; and as a consequence a very weak rotational spectrum is to be expected, a fact which may explain why it has not yet been detected in the interstellar medium.



The structure of triplet propargylene (**2**) poses a puzzling problem. On an UMP2/6-31G** level of theory we had found an ethinylcarbene-like structure with a short and a long CC bond as an energy minimum, but the theoretical IR spectrum calculated within the harmonic approximation did not agree with experiment. The experimental IR spectrum[1d] did not show the typical band for a triple bond stretching vibration around 2000 cm^{-1}. Instead an absorption at 1620 cm^{-1} could be detected. The agreement became much better when a nonrigid structure was taken into account and two vibrations were treated by a nonharmonic approximation. This indicated that propargylene has to be treated as a quasilinear molecule **2c**, in which the positions of the atoms cannot be located exactly, since the activation energy for the reaction $\mathbf{2a} \rightleftarrows \mathbf{2b}$ (both isomers having C_s symmetry) might be smaller than the zero-point energy of the corresponding movement of atoms.



Recently by more sophisticated calculations (QCISD/6-31G*)[1g] a C_2 structure (instead of C_s, as shown in **2c**) with two identical CC bonds has been found to be an energy minimum and gives still better agreement with the experimental spectrum even in the harmonic approximation.

The first detection of **1** was achieved in 1984[5] by matrix isolation IR spectroscopy starting from the precursor molecule **4**. Later we found[6] that the perester **5** is an even better precursor and that matrix-isolated cyclopropenylidene (**1**) can be photochemically isomerized to propargylene (**2**) and vinylidenecarbene (**3**). In 1991 Chen et al.[7] reported the PE spectrum of **1**, which they had generated from 3-chlorocyclopropene (**6**) by thermal HCl elimination. In an independent study we detected the same reaction when we tried to prepare chlorinated cyclopropenylidenes. It turned out that this type of elimination can also be applied to di- and trichlorocyclopropenes and provides a good method for the generation of matrix-isolated mono- and dichlorocyclopropenylidene, which in turn can be isomerized photochemically to the corresponding vinylidenecarbenes and propargylenes. Since it is known from simply substituted carbenes that a halogen atom at the carbene center stabilizes the singlet state by π-electron

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[†] Small Rings. Part 82. For Part 81 see: Maier, G.; Senger, S. *Angew. Chem.*, in press.

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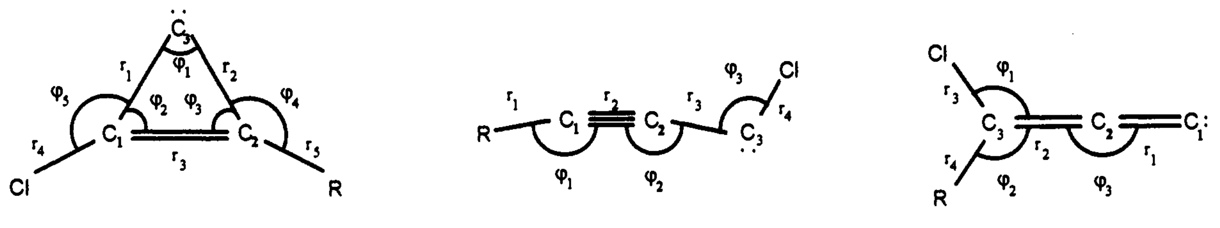
Table 1. Calculated (MP2/6-31G*) Optimum Geometries, Dipole Moments (μ, debye), Rotational Constants (GHz), and Energies (au) of Singlet Cyclopropenylidenes **8** and **12**, Propargylenes **9** and **13**, and Vinylidenecarbenes **10** and **14**

	8 (R = H)	**12** (R = Cl)	**9** (R = H)	**13** (R = Cl)	**10** (R = H)	**14** (R = Cl)
r_1	1.419	1.430	1.068	1.629	1.289	1.286
r_2	1.441	1.430	1.230	1.234	1.335	1.336
r_3	1.327	1.328	1.407	1.401	1.710	1.710
r_4	1.684	1.679	1.715	1.719	1.089	1.710
r_5	1.081	1.679				
φ_1, deg	55.3	55.4	174.1	172.2	124.2	122.9
φ_2, deg		62.3	166.4	163.2	123.6	122.9
φ_3, deg		62.3	110.7	110.9	177.3	180
φ_4, deg	146.8	146.7				
φ_5, deg	147.6	146.7				
μ	2.9	2.3	2.9	2.6	2.8	2.8
A	33.542	10.283	43.830	30.024	42.746	3.504
B	4.106	1.539	3.155	0.957	3.134	3.134
C	3.658	1.539	2.942	0.928	2.919	1.654
E(HF)	–573.51856	–1032.41502	–573.48257	–1032.37206	–573.49019	–1032.38112
E(MP2)	–574.00007	–1033.03025	–573.96640	–1032.98957	–573.97311	–1033.00216



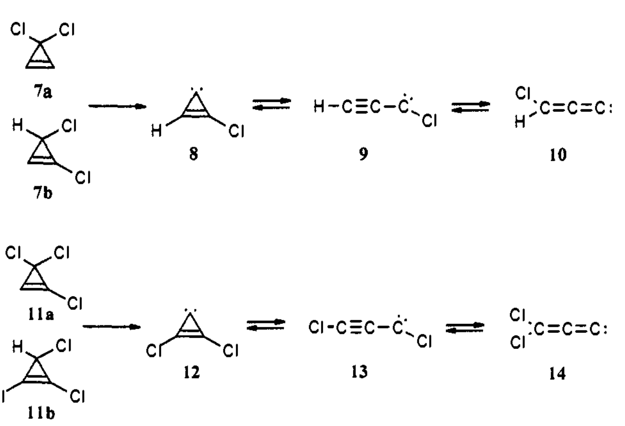
8 , 12 **9 , 13** **10 , 14**

Figure 1. Calculated structures given in Table 1.

donation (CHF, CF_2, CHCl, and CCl_2 have a singlet ground state) it might be expected that the electronic ground state of chlorine-substituted propargylenes would be a singlet rather than a triplet. The influence of fluorine substituents on the structures and energies of C_3F_2 isomers was recently demonstrated by an ab initio calculation.[1e]

Experimental Section

The dichlorocyclopropenes **7a**/**7b** and the trichlorocyclopropenes **11a**/**11b** were synthesized by reduction of tetrachlorocyclopropene with tri-*n*-butyltin hydride[8] followed by preparative gas chromatography. A separation of **7a** from **7b** and **11a** from **11b** was not possible because the positional isomers rapidly interconvert at room temperature. Therefore mixtures of **7a**/**7b** or **11a**/**11b** were subjected to a high-vacuum flash pyrolysis (ca. 10^{-4} mbar, 750–850 °C, quartz tube i.d. 0.8 cm, length 5 cm), and the products were immediately trapped with a high excess of argon on a CsI or BaF_2 window mounted at the cold end of a Displex Closed Cycle Refrigerator (CSA 202, Air Products). For photolyses a Hg super-high-pressure lamp (Osram HBO 200) in connection with a monochromator and a Hg low-pressure lamp with a Vycor or an interference filter were used. FTIR spectra (Bruker IFS 85) were taken in the range 4000–300 cm^{-1} with a resolution of 1.0 cm^{-1}. UV/VIS spectra (190–820 nm, 2 nm resolution) were measured with a diode array spectrometer (HP 8452A) and ESR spectra with a Varian E4 spectrometer.



Calculations

To simplify the identification of carbenes **8**–**10** and **12**–**14** by their infrared spectra, HF/6-31G* and MP2/6-31G* ab initio calculations were performed for the singlet states on the Vanderbilt University VAX 6620 computer using the program GAUSSIAN 92.[9] In each case optimized structures were found by searching for points of zero energy gradient with respect to all internal coordinates. At the energy optima, force constant matrices were computed and diagonalized to give vibrational frequencies in the rigid-rotor harmonic-oscillator approximation. The fact that all frequencies are computed to be real for these zero-gradient structures confirms that they are energy minima. Dipole moment derivatives along normal modes were computed to give infrared intensities in the electrical harmonic approximation. Since the correspondence of the calculated and experimental spectra together with the results of ESR experiments leaves little doubt that the electronic ground states are singlets, no attempts were made to calculate the triplet states. In Table 1 and Figures 1 and 2 energies, optimized geometries, dipole moments, and rotational constants and in Tables 2–7 the calculated IR spectra are given. It is interesting to note that the substitution by chlorine atoms causes a decrease of the dipole moments (compare with the numbers for the parent compounds[1c] **1** (3.4 D), singlet **2** (2.5 D), and **3** (4.1 D)), but they should still be high enough for detection of the chlorocarbenes by microwave spectroscopy.

Results and Discussion

The infrared spectrum of the matrix-isolated pyrolysis products of dichlorocyclopropenes **7a**/**7b** showed—besides small absorptions of the precursor molecules and HCl—a set of new bands which, with the aid of the calculated spectrum, can be assigned to seven of the nine fundamental vibrations of chlorocyclopro-

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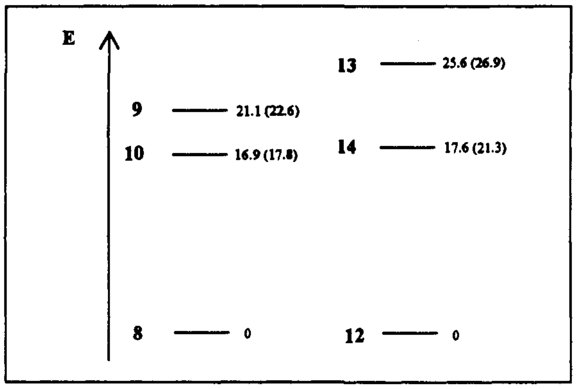

Figure 2. Relative energies (kcal/mol) of chlorine-substituted cyclopropenylidenes **8** and **12**, propargylenes **9** and **13**, and vinylidenecarbenes **10** and **14** in their singlet states: MP2/6-31G* (HF/6-31G*).

Table 2. Calculated and Observed Vibrational Frequencies (cm^{-1}) of Singlet Chlorocyclopropenylidene (**8**), Intensities (Relative to the Strongest Band) in Parentheses

	8	mode		MP2/6-31G*	experiment[a]
ν_1	a′	CH str		3328 (3)	3139.2 (3)
ν_2	a′	ring		1747 (93)	1687.0 (35)
ν_3	a′	ring		1351 (31)	1283.4 (13)
ν_4	a′	ring		1100 (100)[b]	1059.7 (100)
			$^{13}C_3$	-17.8	-16.4
ν_5	a′	CH def		936 (4)	897.2 (2)
ν_8	a″	CH def		883 (16)	883.7 (9)
ν_6	a′	CCl str		597 (19)	580.5 (13)
			^{37}Cl	-7.8	-7.7
ν_9	a″	def		391 (1)	
ν_7	a′	def		365 (9)	

[a] Bands are split due to matrix effects; only the strongest band is given. [b] Abs int 90 km/mol.

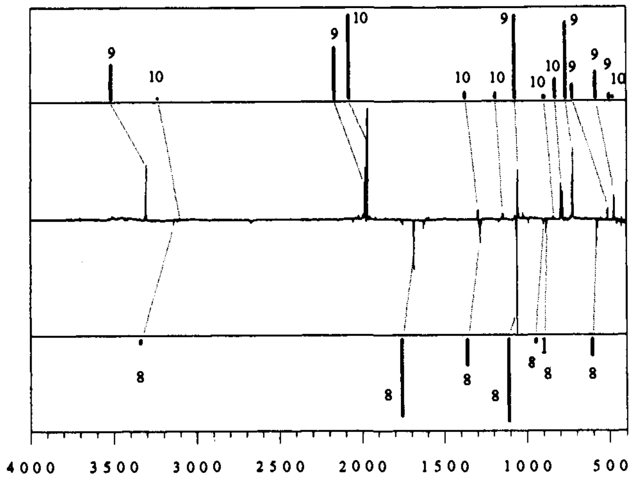

Figure 3. Comparison of experimental (middle) and theoretical (bars at top and bottom) infrared spectra of chlorocyclopropenylidene (**8**), 3-chloropropargylene (**9**), and chlorovinylidenecarbene (**10**). The experimental spectrum (argon matrix) is a difference spectrum of the photoreaction **9**, **10** → **8**.

penylidene (**8**) (Table 2, Figure 3). Only the two low-lying and weak deformation modes ν_7 and ν_9 were not observable. For the strongest band, an "out-of-phase" ring deformation mode observed at 1059.7 cm^{-1} (calc 1100 cm^{-1}), a weak ^{13}C satellite peak (carbenic center C_3), is observable. The shift of −16.4 cm^{-1} is in good agreement with the calculated value of −17.4 cm^{-1}. The CCl stretching vibration of the ^{35}Cl isotopomer is found at 580.5 cm^{-1} (calc 597 cm^{-1}), and the band of the ^{37}Cl isotopomer appears 7.7 cm^{-1} lower (calc −7.8 cm^{-1}) with one-third of the intensity, in accordance with its natural abundance.

Table 3. Calculated and Observed Vibrational Frequencies (cm^{-1}) of Singlet 3-Chloropropargylene (**9**), Intensities (Relative to the Strongest Band) in Parentheses

	9	mode		MP2/6-31G*	experiment[a]
ν_1	a′	CH str		3514 (41)	3305.5 (68)
ν_2	a′	C_2C_3 str		2166 (61)	1983.0 (70)
			$^{13}C_2$	-51.1	-43.4
ν_3	a′	C_1C_2 str		1069 (100)[b]	1054.4 (94)
ν_4	a′	CCl str		763 (91)	725.1 (100)
			^{37}Cl	-3.7	-3.3
ν_8	a″	CH def		724 (15)	511.5 (14)
ν_5	a′	CH def		584 (31)	475.4 (36)
ν_6	a′	def		504 (3)	
ν_9	a″	def		295 (<1)	
ν_7	a′	def		197 (2)	

[a] Bands are split due to matrix effects; only the strongest band is given. [b] Abs int 162 km/mol.

Table 4. Calculated and Observed Vibrational Frequencies (cm^{-1}) of Singlet Chlorovinylidenecarbene (**10**), Intensities (Relative to the Strongest Band) in Parentheses

	10	mode		MP2/6-31G*	experiment[a]
ν_1	a′	CH str		3234 (<1)	3103.5 (1)
ν_2	a′	CCC str		2080 (100)[b]	1967.6 (100)
			$^{13}C_3$	-7.8	-7.7
			$^{13}C_1$	-18.2	-16.4
			$^{13}C_2$	-53.9	-50.4
ν_3	a′	CH def		1373 (6)	1293.0 (7)
ν_4	a′	CCC str		1188 (5)	1146.5 (4)
ν_8	a″	CH def		895 (1)	839.9 (1)
ν_5	a′	CCl str		826 (22)	794.1 (40)
			^{37}Cl	-4.3	-4.4
ν_6	a′	CCC def		481 (1)	
ν_9	a″	CCC def		217 (<1)	
ν_7	a′	def		166 (<1)	

[a] Bands are split due to matrix effects; only the strongest band is given. [b] Abs int 709 km/mol.

Chlorocyclopropenylidene (**8**) exhibits a weak UV absorption with two maxima at 270 and 260 nm. This is roughly the same position as found for the unsubstituted cyclopropenylidene (**1**). Irradiation of the matrix with 254-nm light from a Hg low-pressure lamp leads to a fast decrease of this band and of the above mentioned IR absorptions and to an increase of two new sets of IR bands belonging to 3-chloropropargylene (**9**) and to chlorovinylidenecarbene (**10**). From the rate of appearance of the bands during the course of the photolysis it can be concluded that **10** is formed via **9**. In the UV region both molecules **9** and **10** have broad and overlapping absorption bands between 270 and 300 nm, which are slightly more intense than those of **8**. The photochemical back reaction (**9**, **10** → **8**) could be induced by changing the excitation wavelength to 280–310 nm (Hg high-pressure lamp, monochromator). A difference IR spectrum monitoring this reaction is given in Figure 3.

Assignment of the IR bands of **9** (Table 3) and **10** (Table 4) follows from the calculated spectra. The most interesting feature in the spectrum of 3-chloropropargylene (**9**) is the presence of two strong bands at 3305 (calc 3514 cm^{-1}) and 1983.0 cm^{-1} (calc 2166 cm^{-1}), which are both typical for the CH and CC stretching vibration of an ethinyl group. For the latter band a weak ^{13}C satellite peak can be detected. The shift of −43.4 cm^{-1} corresponds well with the calculated shift for the $^{13}C_2$ isotopomer (−51.1 cm^{-1}). Absorption of the $^{13}C_1$ species (calc shift −25 cm^{-1}) is obscured by the intense ν_2 band of **10**, and that of the $^{13}C_3$ isotopomer (calc shift −1 cm^{-1}) cannot be resolved. The strong band for the C_2–C_3 stretching mode is found at 1054.4 cm^{-1} (calc 1069 cm^{-1}). The CCl stretching vibration lies at 725.1 cm^{-1} (calc 763 cm^{-1}) and shows a shift of −3.3 cm^{-1} for the ^{37}Cl isotopomer (calc −3.7 cm^{-1}).

The most prominent IR band of chlorovinylidenecarbene **10**, the "out-of-phase" CCC stretching vibration, is found at 1967.6

Table 5. Calculated and Observed Vibrational Frequencies (cm^{-1}) of Singlet Dichlorocyclopropenylidene (**12**), Intensities (Relative to the Strongest Band) in Parentheses

	12	mode		MP2/6-31G*	experiment^a
$\nu_8 + \nu_7{}^b$	a_1				1793.5 (6)
			$^{35}Cl/^{37}Cl$		−2.9
			$^{37}Cl/^{37}Cl$		−5.3
$\nu_1{}^b$	a_1	ring		1828 (17)	1736.6 (14)
$\nu_4 + \nu_7$	b_2				1268.5 (5)
ν_2	a_1	ring		1329 (10)	1263.2 (5)
$\nu_7 + \nu_3$	b_2				1210.2 (6)
			$^{35}Cl/^{37}Cl$		−6.6
			$^{37}Cl/^{37}Cl$		−13.4
ν_7	b_2	ring		1142 (100)^c	1095.9 (100)
			$^{13}C_3$	−5.8	−5.8
			$^{13}C_{1/2}$	−19.2	−17.9
					824.4 (2)
ν_8	b_2	CCl str		706.9 (10)	681.7 (10)
			$^{35}Cl/^{37}Cl$	−2.8	−2.9
			$^{37}Cl/^{37}Cl$	−5.8	−5.8
ν_3	a_1	CCl str		545.1 (2)	527.5 (1)
			$^{35}Cl/^{37}Cl$	−4.8	−4.4
ν_5	a_2	def		535.1 (0)	
ν_9	b_2	def		454.0 (1)	
ν_6	b_1	def		267.8 (4)	
ν_4	a_1	def		166.0 (<1)	

[a] Bands are split due to matrix effects; only the strongest band is given. [b] Perturbed by Fermi resonance. [c] Abs int 298 km/mol.

Table 6. Calculated and Observed Vibrational Frequencies (cm^{-1}) of Singlet Dichloropropargylene (**13**), Intensities (Relative to the Strongest Band) in Parentheses

	13	mode		MP2/6-31G*	experiment^a
ν_1	a′	C_1C_2 str		2248 (100)^b	2079.9 (100)
			$^{13}C_1$	−41.6	−37.6
			$^{13}C_2$	−43.9	−39
ν_2	a′	C_2C_3 str		1226 (18)	1192.8 (16)
ν_3	a′	C_3Cl str		777 (73)	743.0 (70)
			$^{37}ClC_1$	−1.3	−1.5
			$^{37}ClC_3$	−4.2	−3.4
			$^{37}Cl/^{37}Cl$	−5.6	−5.4
ν_4	a′	C_1Cl + def		685 (3)	
ν_5	a′	def		420 (<1)	
ν_8	a″	def		382 (<1)	
ν_6	a′	def		272 (<1)	
ν_9	a″	def		178 (1)	
ν_7	a′	def		106 (<1)	

[a] Bands are split due to matrix effects; only the strongest band is given. [b] Abs int 435 km/mol.

cm^{-1} (calc 2080 cm^{-1}) with an enormous absorption intensity that easily allows the detection of all three ^{13}C isotopomers. Observed shifts (C_3, −7.7 cm^{-1}; C_1, −16.4 cm^{-1}; C_2, −50.4 cm^{-1}) are in good agreement with calculated values (C_3, −7.8 cm^{-1}; C_1, −18.2 cm^{-1}; C_2, −53.9 cm^{-1}). The second strongest band at 794.1 cm^{-1} (calc.: 826 cm^{-1}) is mainly a CCl stretching vibration, with a ^{37}Cl isotopic shift of −4.4 cm^{-1} (calc −4.3 cm^{-1}).

An analogous experiment was carried out for the trichlorocyclopropenes **11a**/**11b**. High-vacuum flash pyrolysis at 800 °C yielded HCl and dichlorocyclopropenylidene (**12**). A set of nine IR bands could be recorded for this compound (Table 5). Five of them, the ring vibrations ν_1, ν_2, and ν_7 and the two CCl stretching vibrations ν_3 and ν_8, are fundamental bands. Three absorptions are combination bands involving the very intense ν_7 vibration. Only a very weak absorption at 824.4 cm^{-1} remains unassignable. Four fundamental modes, the IR inactive ν_5 and the very weak and low-lying ν_4, ν_6, and ν_9, could not be found in the experimental spectrum. ν_1, which mainly is the CC double bond vibration, is perturbed by a Fermi resonance with the $\nu_7 + \nu_8$ combination. From the intensity ratio the approximate positions of the unshifted bands are calculated to be 1756 (ν_1) and 1773 ($\nu_7 + \nu_8$). Relative intensities of the observed bands of the ^{13}C isotopomers (ν_7) and ^{37}Cl isotopomers (ν_3, ν_8) are in accordance with a C_{2v} symmetry of the molecule. Their frequency shifts agree well with the calculated values.

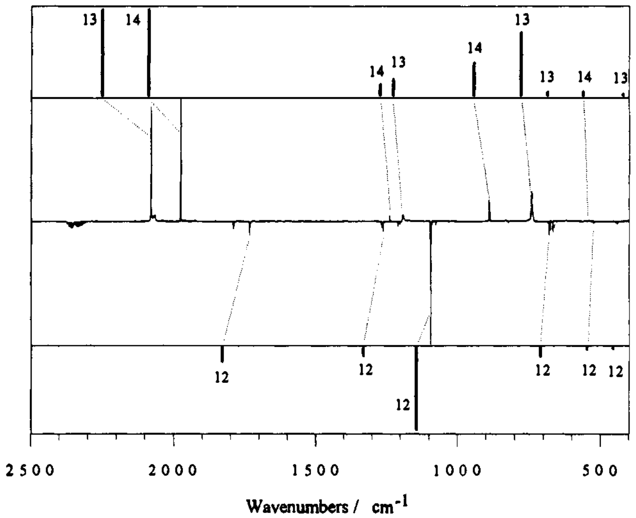

Figure 4. Comparison of experimental (middle) and theoretical (bars at top and bottom) infrared spectra of dichlorocyclopropenylidene (**12**), dichloropropargylene (**13**), and dichlorovinylidenecarbene (**14**). The experimental spectrum (argon matrix) is a difference spectrum of the photoreaction **13**, **14** → **12**.

Table 7. Calculated and Observed Vibrational Frequencies (cm^{-1}) of Singlet Dichlorovinylidenecarbene (**14**), Intensities (Relative to the Strongest Band) in Parentheses

	14	mode		MP2/6-31G*	experiment^a
$\nu_1 + \nu_2$	a_1				3201.4 (2)
$\nu_1 + \nu_3$	a_1				2518.2 (1)
				$^{35}Cl/^{37}Cl$	−3.9
				$^{35}Cl/^{37}Cl$	−7.3
ν_1	a_1	CCC str		2086 (100)^b	1976.7 (100)
			$^{13}C_3$	−8.0	−8.6
			$^{13}C_1$	−18.8	−16.3
			$^{13}C_2$	−53.9	−49.6
ν_2	a_1	CCC str		1271 (12)	1238.1 (10)
ν_7	b_2	ClCCl str		942 (38)	890.5 (38)
			$^{35}Cl/^{37}Cl$	−1.6	−1.9
			$^{37}Cl/^{37}Cl$	−3.2	−3.4
			$^{13}C_3$	−32.4	−28.9
ν_5	b_1	def		578 (0)	
ν_3	a_1	ClCC def		560 (3)	542.9 (6)
			$^{35}Cl/^{37}Cl$	−4.4	−3.4
			$^{37}Cl/^{37}Cl$	−8.9	−9.7
ν_8	b_2	CCC def		494 (0)	
ν_4	a_1	ClCCl def		314 (0)	
ν_6	b_1	CCC def		181 (1)	
ν_9	b_2	CCC def		145 (<1)	

[a] Bands are split due to matrix effects; only the strongest band is given. [b] Abs int 916 km/mol.

In the UV spectrum of **12** two weak absorption bands at 268 and 258 nm are present. On irradiation of the matrix with 254-nm light (Hg low-pressure lamp) **12** is isomerized to the dichloropropargylene (**13**) and dichlorovinylidenecarbene (**14**). They both absorb light between 275 and 320 nm (two strongly overlapping bands). Subsequent photolysis with light corresponding to these two absorptions (Hg high-pressure lamp, monochromator) initiates the reformation of the cyclopropenylidene **12**. A difference IR spectrum monitoring this reaction (Figure 4) shows the bands of **12**, **13**, and **14**.

With the help of calculated spectra three of the bands of dichloropropargylene (**13**) can be assigned to the ν_1–ν_3 fundamentals. The strongest band at 2079.9 cm^{-1} (calc 2248 cm^{-1}) is a nearly pure C_1C_2 triple bond vibration. Two weak ^{13}C satellite bands (C_1, −37.6 cm^{-1}, calc −41.6 cm^{-1}; C_2, −39.0 cm^{-1}, calc −43.9 cm^{-1}) are observable at only slightly different positions. The other strong band of **13** at 743.0 cm^{-1} (calc 777 cm^{-1}) is one of the two CCl stretching vibrations. Its splitting by the chlorine isotopes is not fully resolved, but it is in qualitative agreement with the calculation. The remaining six fundamentals are predicted to be very weak and are not observable in the spectrum.

As expected, the strongest band of dichlorovinylidenecarbene (**14**) (Table 7) for the "out-of-phase" CCC stretching vibration is found at 1976.7 cm^{-1} (calc 2086 cm^{-1}). Bands of all three ^{13}C isotopomers are seen at the calculated positions. The corresponding "in-phase" CCC stretching vibration appears at 1238.1 cm^{-1} (calc 1271 cm^{-1}). The "out-of-phase" CCl stretching vibration gives rise to the second strongest band at 890.5 cm^{-1} (calc 942 cm^{-1}). All three bands arising form the 35/35, 35/37, and 37/37 combinations of the chlorine isotopes in natural abundance can be detected. Even the $^{13}C_3$ isotopomer is observable as a very weak band shifted by −28.9 cm^{-1} (calc −32.4 cm^{-1}). The "in-phase" CCl vibration is found at 542.9 cm^{-1} (calc 559 cm^{-1}) and has a very low intensity. Chlorine isotopomers can also be observed. Five other fundamentals are predicted either to be IR inactive or to give only very weak and low-lying bands and accordingly cannot be observed.

Conclusion

The main structural information that can be drawn from the infrared spectra of propargylenes **9** and **13** is that, in contrast to the unsubstituted triplet propargylene (**2**), chloro derivatives have singlet ground states with "fixed" CC triple and CC single bonds. The expected ground states for the propargylenes **9** and **13** were confirmed by ESR spectroscopy. Under the same experimental conditions where **2** showed an intense triplet signal (254-nm irradiation of **1**, prepared by pyrolysis of **5**) no such absorptions could be recorded for the chlorine-substituted propargylenes **9** and **13**.

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