Carbon-13 Nuclear Magnetic Resonance Spectral Properties of Alkenylidenecyclopropanes

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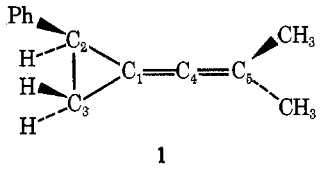
The ^{13}C chemical shifts in a series of alkenylidenecyclopropanes have been measured and have been assigned to specific carbon atoms and substituent shift effects have been analyzed. A comparison of the ^{13}C chemical shifts in the alkenylidenecyclopropanes with those in allenes and methylenecyclopropanes reveals considerable differences in the chemical shifts of the ring and allene carbon atoms. The internal carbons (C_1 and C_4) of alkenylidenecyclopropanes are strongly shielded relative to the corresponding carbon atoms in allenes and methylenecyclopropanes, while the terminal allene and ring carbons are deshielded. These effects are postulated to arise from a strong conjugative interaction between the in-plane (relative to the three-membered ring) C_4–C_5 π bond with the Walsh-type orbitals of the three-membered ring.

Recent chemical studies with alkenylidenecyclopropanes,[2,3,4] methylenecyclopropanes,[4,5] and vinylcyclopropanes[6] have revealed substantial differences in reactivity and mode of reaction with the cycloaddition reagents 4-phenyl-1,2,4-triazoline-3,5-dione[2,4,6] (PTAD) and chlorosulfonyl isocyanate.[3,5] The reactivity and mode of reaction of the alkenylidenecyclopropanes have been interpreted in terms of an interaction between the Walsh-type orbitals[7] of the three-membered ring and the C_4–C_5 π bond which is not present in the methylene- or vinylcyclopropanes, a rationale which has been supported by preliminary theoretical calculations.[2] In a continuing study of the chemical and physical properties of such systems we have completed a study of the ^{13}C NMR spectral properties of alkenylidenecyclopropanes for comparison with allenes and methylenecyclopropanes. Articles describing the results of studies on the bonding in alkenylidenecyclopropanes using photoelectron spectroscopic and theoretical techniques,[8] and a kinetic study of the cycloaddition reaction with PTAD[9] have already appeared.

Results and Discussion

Assignment of Chemical Shifts.[10] Assignment of the resonances to specific carbons in the alkenylidenecyclopropanes has been accomplished on the basis of multiplicities in nondecoupled spectra, the magnitudes of the coupling constants, the absolute values of the chemical shifts, and substituent shift effects. Initial chemical shift assignments were based on the complete analysis of the nondecoupled spectra of 1 and 2. The methyl groups attached to C_5 in 1 appear as quartets at δ 22.3 and 22.8 with J values of 126 Hz typical for methyl groups. The higher field resonance has been tentatively assigned to the methyl cis to the phenyl on the basis of the observed shielding of the α-carbon atoms in cis alkenes relative to trans alkenes ($\Delta\delta$ ~6 ppm) which has been attributed to steric polarization.[11,12] The methyl resonances of the other isobutenylidenecyclopropanes reported in this article consistently fall in the range δ 21.3–22.8. The resonance of C_2 appears as a doublet (δ 26.9, J = 171 Hz), while that for C_3 appears as a triplet (δ 18.4, J = 168 Hz). The larger values for these coupling constants are typical of those observed in cyclopropane derivatives.[13a] The aromatic ^{13}C resonances were assigned on the basis of their multiplicities, the ipso carbon appearing as a lower field singlet, the ortho carbons as a double doublet, and the meta and para carbons as double triplets (see Table I for specific values of the coupling constants).



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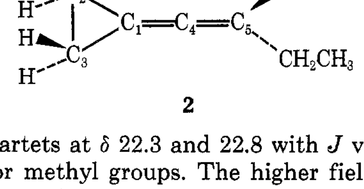

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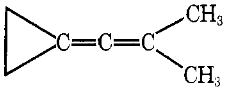
The assignment of the resonances of C_1, C_4, and C_5 were made by comparison of the shifts of these carbons in 1 and 2. The substitution of methyl by ethyl results in a deshielding of C_5 (δ 102.3 to 113.8; i.e., a β substituent effect),[14] a shielding of C_4 (δ 189.8 to 186.9; a γ substituent effect),[14] and a deshielding of C_1 (δ 83.5 to 87.0; a δ substituent effect).[14] The much lower field resonance of C_4 is consistent with those observed for the central carbons of allenes.[15] The resonances in the spectra of the other alkenylidenecyclopropanes were assigned by comparison with those in 1 and applying known trends in substituent shifts.[13b]

Analysis of Substituent Effects in Alkenylidenecyclopropanes. In order to estimate the ^{13}C chemical shifts in the parent alkenylidenecyclopropane 3[16] for comparison with the ^{13}C chemical shifts in allenes and methylenecyclopropanes it is necessary to carry out a detailed analysis of the substituent shift effects in the alkenylidenecyclopropanes. The introduction of a methyl group in 1 at C_3 trans to the phenyl (i.e., 5) produces a β-alkyl shift at C_2 of +4.5 ppm whereas in the cis compound 6 the shift is +1.8 ppm indicating a steric shift of −2.7 ppm. In the polymethyl series 7–11 the β-alkyl shift is +4.6 to +5.3 ppm with a much smaller apparent steric shift of ~−0.6 ppm. Similar, but larger, α and β steric shifts are observed at C_2 (or C_3) (see Table II).



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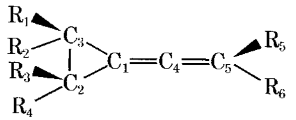
Substantial steric shifts of the resonances of the methyl carbons are observed in the *cis*- and *trans*-methylphenyl ($\Delta\delta$ 6.0 ppm between 5 and 6) and dimethyl compounds ($\Delta\delta$ 5.3 ppm between 7 and 8), values of $\Delta\delta$ which compare very closely with those observed between the α carbons of cis and trans alkenes ($\Delta\delta$ ~6 ppm).[11]

Comparison and Analysis of the ^{13}C Chemical Shifts in Alkenylidenecyclopropanes, Tetramethylallene, Methylenecyclopropane, and 2-Methylpropene. In order to adequately compare the ^{13}C chemical shifts of alk-

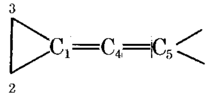
Table I. ^{13}C Chemical Shifts in



					δ^a										
Compd	R_1	R_2	R_3	R_4	C_1	C_2	C_3	C_4	C_5	R_1	R_2	R_3	R_4	$R_5{}^h$	$R_6{}^h$
1	C_6H_5	H	H	H	83.5	18.4	26.9	189.8	102.3	*b*				22.3	22.8
						(168)	(171)							(126)	(126)
2	C_6H_5	H	H	H	87.0	19.1	25.6	186.9	113.8	*c*				CH_2: 28.3	28.4
						(165)	(170)							(128)	(128)
														CH_3: 14.8	14.8
														(125)	(125)
4[d]	C_6H_5	H	H	H	85.9	22.2	26.2	189.0	108.3	*d*				19.4	CH_2: 30.3, 30.3
					86.3			189.3	108.4					19.7	CH_3: 14.9, 14.8
5[e]	C_6H_5	H	H	CH_3	88.0	26.0	32.1	187.1	99.2	*e*			18.2	21.4	21.5
6	C_6H_5	H	CH_3	H	85.3	21.8	28.3	188.3	99.1	*f*		12.26		21.2	21.4
												(128)		(127)	(127)
7[g]	CH_3	H	H	CH_3	88.6	22.5	22.5	186.3	97.7	18.0			18.0	21.7	21.7
8[g]	CH_3	H	CH_3	H	88.0	18.1	18.1	186.2	97.9	12.7		12.7		21.4	21.9
9	CH_3	CH_3	H	H	87.8	20.8	24.6	185.7	98.0	24.6	24.6			21.5	21.5
						(165)				(125)	(125)			(127)	(127)
10	CH_3	CH_3	CH_3	H	92.7	24.2	26.6	184.7	97.1	26.4	26.6	19.0		21.7	22.0
						(162)				(122)	(122)	(129)		(127)	(127)
11	CH_3	CH_3	CH_3	CH_3	98.0	28.4	28.4	184.5	97.4	22.8	22.8	22.8	22.8	22.6	22.6
										(129)	(129)	(129)	(129)	(125)	(125)

[a] Values in parentheses under the δ's are *J*'s in hertz when determined. [b] Aromatic peaks at δ 128.7 (dt, $J = 157$, 7.3 Hz), 129.1 (dt, $J = 162$, 7.3 Hz), 131.9 (dd, $J = 162$, 7.3 Hz), 144.3 (s). [c] Aromatic peaks at δ 127.3 (dt, $J = 159$, 7 Hz), 127.7 (dt, $J = 159$, 7 Hz), 129.6 (dd, $J = 158$, 7 Hz), 142.9 (s). [d] Coupling constants were not determined. See ref 12. Aromatic peaks at δ 128.7, 129.1, 131.9, 144.3. [e] Coupling constants were not determined. Aromatic resonances at δ 126.1, 126.8, 128.1, and 141.9. [f] Aromatic peaks at δ 126.5 (dt, $J = 158$, 6 Hz), 128.2 (dt, $J = 157$, 6 Hz), 129.6 (dd, $J = 152$, 6 Hz), 137.7. [g] Coupling constants were not determined. [h] CH_3 except in compound 4.

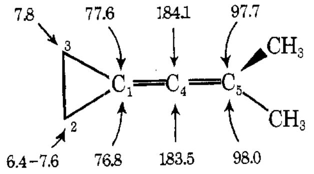
Table II. Substituent and Steric Shifts (ppm) in



Carbon atom (compds)	α effect	α steric effect	β effect	β steric effect	γ effect	δ effect
C_1 (4–6)			+4.5	−2.7		(+0.9 to +2.6)[a]
(7–11)			+4.6 to +5.3	−0.6		
C_2 (or C_3) (4–6)	+7.6	−4.2	+4.2	−2.8		
(7–11)	+8.5	−4.4	+6.1 to +6.4	−4.0 to −4.4		
C_4 (4–6)					−2.7[b] (+1.2)[c]	
(7–11)					−1.0 to −1.6[d]	
C_5 (4–6)			+5.7 to +6.0		*e*	

[a] Parenthesized shifts arising from substituent changes at the allene terminus. + shifts indicate shifts to lower field, — shifts to higher field. [b] Apparent steric shift of +1.2 ppm. [c] Apparent steric shift of —0.7 to —2.2 ppm. [d] Apparent steric shift is less than the limits of experimental uncertainty. [e] Substituent shift is less than the limits of experimental uncertainty.

enylidenecyclopropanes with those in allenes and methylenecyclopropanes one must derive chemical shifts for compounds of comparable substitution.[16] Starting with **7** and **9**, neither of which are complicated by cis steric effects, and using the substituent shifts given in Table II the ^{13}C chemical shifts of **3** are estimated to be those shown below (the δ's above the structure are derived by extrapolation from **7**, those below from **9**).



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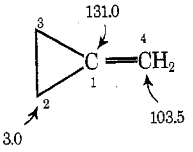

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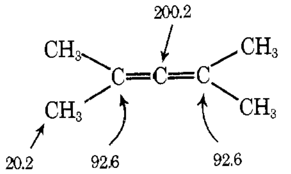

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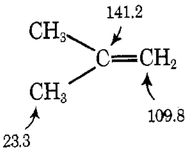

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The effect of the three-membered ring on the ^{13}C chemical shifts in **3** can be estimated by comparing the chemical shifts of 2-methylpropene (**13**) and methylenecyclopropane[17] (**12**). Formation of the three-membered ring results in a shielding of the saturated carbon atoms (20.3 ppm) and a deshielding of the vinyl carbons (10.2 ppm on going from C_2 of **13** to C_1 of **12**, and 6.3 ppm on going from C_1 of **13** to C_4 of **12**). Should similar changes in chemical shifts occur in the transformation of tetramethylallene (**14**) to **3**, one would expect the values of the chemical shifts to be $\delta_{C_2(C_3)}$ −0.1, δ_{C_1} 82.4, and δ_{C_4} 193.9. Comparison of these values with those observed in **3**, along with a comparison of the chemical shift of a terminal allene carbon of **14** with that of C_5 in **3**, reveals that C_1 and C_4 experience additional shielding of 4.8–5.6 ppm at C_1 and 9.8–10.4 ppm at C_4 in **3**, while $C_2(C_3)$ and C_5 experience additional deshielding of 6.5–7.9 ppm at $C_2(C_3)$ and 5.1–5.4 ppm at C_5.

An analysis of the bonding in **3** provides a possible explanation for the observed shielding of C_1 and C_4 in the alkenylidenecyclopropanes. A reasonably strong interaction exists between the in-plane C_4–C_5 π bond and the Walsh-type orbitals of the three-membered ring[2,8] (estimated to be approximately 80% that in 1,3-butadiene[8]) which results in considerable triple bond character in the C_1–C_4 bond with concomitant weakening of the C_4–C_5 π and C_1–C_2 (C_1–C_3) σ bonds. CNDO calculations indicate bond orders of 0.9291 for the C_4–C_5 π bond, 0.3504 for the C_1–C_4 in-plane "π bond" interaction, 0.9192 for the exocyclic double bond, and 0.9043 for the C_1–C_2 (C_1–C_3) σ bond. This added electron density, or "triple bond" character of the C_1–C_4 bond apparently results in shielding of C_1 and C_4 comparable to that observed in alkynes which appear at 40–60 ppm higher field than the sp^2-hybridized carbons of alkenes.[18] The deshielding of C_2 (C_3) and C_5 appears to be the result of lowered electron density at these carbon atoms. Studies are currently under way on the synthesis and physical properties of alkenylidenecyclobutanes, -cyclopentanes, and -cyclohexanes for comparison with the alkenylidenecyclopropanes.

Registry No.—**1,** 4544-23-4; **5,** 33530-27-7; **6,** 33530-26-6; **7,** 37817-46-2; **8,** 37817-36-0; **9,** 28438-32-6; **10,** 14803-30-6; **11,** 13303-30-5.

References and Notes

(1) Supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.
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