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APPLICATIONS OF NUCLEAR QUADRUPOLE RESONANCE TO ORGANIC CHEMISTRY. TETRACHLOROCYCLOPROPENE AND RELATED COMPOUNDS

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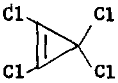
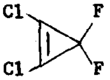
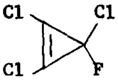
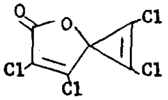
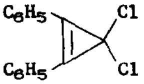
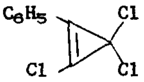
The ^{35}Cl nuclear quadrupole resonance (nqr) spectra of tetrachlorocyclopropene (C_3Cl_4, 1) and trichlorocyclopropenium tetrachloroaluminate ($C_3Cl_3^+$, $AlCl_4^-$) were reported recently by Lucken and Mazeline.[1] Two groups of resonances were observed for 1 (see Table I), the lower frequency bands being attributed to the vinylic chlorines by reference to cis-1,2-dichloroethylene (34.97 and 35.03 MHz at 20°K) and the higher frequency bands being assigned to the gem-dichloride group by comparison with 1,1-dichlorocyclopropane (36.61 MHz). Both sets of the tetrachlorocyclopropene bands occurred at higher frequencies than those of the model compounds, presumably because of the electron-withdrawing properties of the gem-dichloride and dichlorovinyl groups respectively.[1,2]

Recent work in our laboratories[3] has led to the synthesis of a number of polychlorinated cyclopropenes which are more suitable reference compounds for 1. The nqr data for representative compounds, given in Table I, indicate that the previous assignments[1] for 1 are incorrect and should be reversed. The assignments for all of the compounds in the Table (except 1 and the spirolactone) are unambiguous; the structures for these compounds are all well established, and in the cases where both vinyl and geminal chlorines are present assignment of the nqr lines is easily made from the relative intensities. The indicated assignments for the spirolactone are consistent with existing data for five-membered ring compounds,[4a] and with the fact that the cyclopropene chlorines are symmetrically equivalent. Chlorines in the vinyl positions of the model cyclopropenes give resonances in the narrow range 38.0-38.8 MHz, whereas chlorines in the $>CCl_2$ group resonate at 34.8-35.7 MHz at 77° K. The lines for 1 at 38.2-38.8 MHz therefore must be due to the vinyl chlorines, and those at 36.4-36.7 MHz are consistent with a gem-dichloride assignment. It is noteworthy that the vinyl chlorines of 1,2-dichloro-3,3-difluorocyclopropene and 1,2,3-trichloro-3-fluorocyclopropene give patterns almost identical to that for the vinyl chlorines of 1, and that the "geminal"

TABLE I

NQR Spectra of Selected Cyclopropenes

Structure	Type of Chlorine	Resonant Frequencies[a] at 77°K
 [b]	Vinylic	38.24, 38.26, 38.51, 38.74
	Geminal	36.41, 36.73
	Vinylic	38.14, 38.37, 38.58, 38.75
	Vinylic	38.15(1/2), 38.38(1/2), 38.65(1)
	"Geminal"	36.08(1/2), 36.34(1/2)
	Vinylic	38.62(1), 38.77(1)
	Vinylic[c]	36.54(1), 37.97(1)
	Geminal	34.78, 35.02
	Vinylic	37.71(1)
	Geminal	35.17(1), 35.71(1)

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[a] Resonant frequencies are given in MHz; numbers in parentheses indicate relative number of chlorines. Previously unpublished spectra were obtained on the Wilks NQR-1A commercial spectrometer, with frequencies measured using a Northeastern Engineering Model 14-21C frequency counter.

[b] Ref. 1.

[c] Chlorines on five-membered ring; see ref. 4a.

chlorine of the fluorotrichlorocyclopropene absorbs at frequencies very near those for the geminal chlorines of **1**.

In cyclopropenes the vinyl halogens come into resonance at *higher* frequencies, and the geminal chlorines at *lower* frequencies, than is the case for chlorinated four-, five-, six-, and seven-membered rings.[4] The order is in fact reversed from that observed in larger rings; for example, the vinyl halogens in hexachlorocyclopentadiene are observed at 36.9-37.5 MHz, while the geminal chlorines are found at 38.1-39.1 MHz.[5] The reversal of the usual order in tetrachlorocyclopropene may be due in part to a contribution of the ionized form, $C_3Cl_3^+Cl^-$, to the ground state of **1**. This would increase the polarity of the geminal C-Cl bonds, reducing the quadrupole coupling constant and the resonant frequency.[2] The resulting increased electronegativity of the carbon atoms in the ring would decrease the polarity of the bonds to the vinyl chlorines, increasing the resonant frequency.* In agreement with this interpretation, successive substitution of the vinyl chlorines by phenyl, which should favor cyclopropenium ion character in the ring, further lowers the resonant frequency for the geminal chlorines.

A more detailed study of the nqr spectra of polychlorinated cyclic compounds is in progress and will be reported subsequently.

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*Other factors, such as unusual hybridization at carbon in cyclopropenes, a higher degree of C-Cl π-bonding due to contributions of the ionized form,[1] and the electronegativity of other substituents may also affect the resonant frequencies.

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