halides.[5,6] It is likely that the halogen acid is required to produce a halonickel dicarbonyl hydride which is the true catalyst. (Other acids could produce analogous hydrides.)

$$HX + Ni(CO)_4 \rightleftharpoons HNi(CO)_2X + 2CO$$

The hydride could then add to the olefin (or acetylene) to give an alkylnickel dicarbonyl halide; this could absorb carbon monoxide and form the acylnickel dicarbonyl halide. The final step could either be elimination of acyl halide with the re-formation of nickel carbonyl, or possibly direct alcoholysis of the acyl compound to ester (or acid) and the halonickel dicarbonyl hydride.

$$HNi(CO)_2X + RCH{=}CH_2 \longrightarrow RCH_2CH_2Ni(CO)_2X \left(+ \underset{}{RCHCH_3}\overset{Ni(CO)_2X}{|} \right)$$

$$RCH_2CH_2Ni(CO)_2X + CO \longrightarrow RCH_2CH_2CONi(CO)_2X$$

$$RCH_2CH_2CONi(CO)_2X + 2CO \longrightarrow RCH_2CH_2COX + Ni(CO)_4$$

$$RCH_2CH_2COX + R'OH \longrightarrow RCH_2CH_2COOR' + HX$$

or $$RCH_2CH_2CONi(CO)_2X + R'OH \longrightarrow RCH_2CH_2COOR' + HNi(CO)_2X$$

An alternative initial step would be the formation, from the halogen acid and olefin, of alkyl halide which then reacts directly with nickel carbonyl, as allylic halides do,[7] to produce alkylnickel dicarbonyl halides.

$$RX + Ni(CO)_4 \longrightarrow RNi(CO)_2X + 2CO$$

Both of these initial steps have analogies in other group VIII metal reactions. Hydrogen chloride adds to bis-(triphenylphosphine)-carbonyl chloroiridium to give bis-(triphenylphosphine)-carbonyl dichloroiridium hydride[8] and methyl iodide adds to bis-(triethylphosphine)-iodo-(methyl)-platinum to form bis-(triethylphosphine)-diiodo-(dimethyl)-platinum.[9] In either case, the subsequent steps are similar to those proposed to explain the hydroformylation reaction,[10] with hydrolysis or alcoholysis replacing hydrogen reduction.

Attempts to detect intermediates in the olefin or acetylene carboxylation reactions have not been successful because the nickel carbonyl does not react with hydrogen halides or alkyl halides at low temperatures. At higher temperatures, the intermediates react further as they are formed and cannot be observed.

(7) E. O. Fischer and G. Burger, *Z. Naturforsch.*, **16b**, 77 (1961); *Chem. Ber.*, **94**, 2409 (1961).
(8) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).
(9) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).
(10) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

RESEARCH CENTER
HERCULES POWDER COMPANY
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RICHARD F. HECK

RECEIVED APRIL 5, 1963

Variation of Vinyl Proton Coupling Constants with Ring Size in *cis*-Cyclic Olefins

Sir:

Calculations based on the Karplus equation relating dihedral angle and coupling constant suggest that all *cis*-disubstituted olefins (dihedral angle 0°) should show vinyl proton coupling constants of 6.1 c.p.s. while *trans*-disubstituted olefins (dihedral angle 180°) should show vinyl proton coupling constants of 11.9 c.p.s.[1] The ratio of J_{cis}/J_{trans} is consistent with the experimental for ethylene[2] but the predicted values[3] are substantially

(1) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(2) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A269**, 385 (1962).
(3) The agreement is improved by consideration of σ–π interaction which adds 1.5 c.p.s. to the predicted values: M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

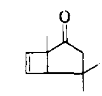
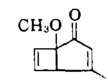
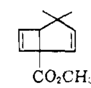
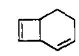
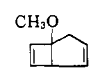
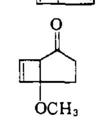
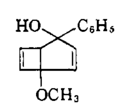
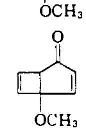
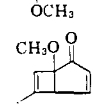
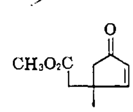
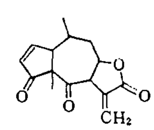
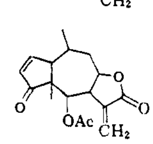
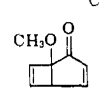
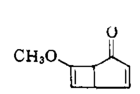
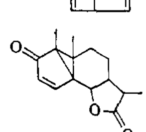
TABLE I

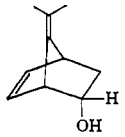
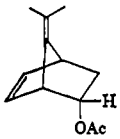
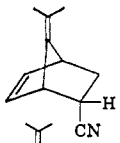
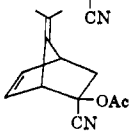
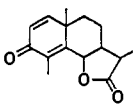
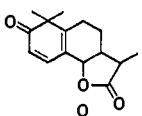
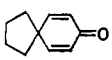
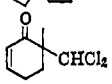
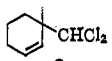
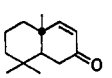
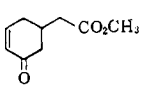
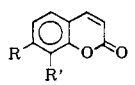
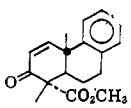
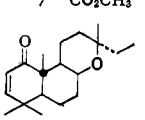
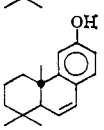
SUMMARY OF VARIATION OF VINYL PROTON COUPLING CONSTANT WITH RING SIZE IN *cis*-CYCLIC OLEFINS

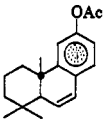
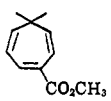
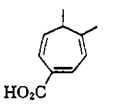
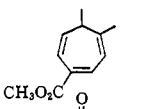
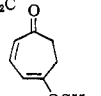
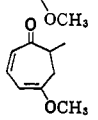
Ring size	Range of coupling constants	No. of examples
8	11.8–12.8	3
7	9.7–12.5	6
6	9.9–10.5	15
5	5.4– 7.0	16
4	2.5– 3.7	8

TABLE II

VINYL PROTON COUPLING CONSTANTS OF *cis*-CYCLIC OLEFINS

Structure	Ring size	$J_{vinyl\ protons}$ (c.p.s.)[a]
	4	2.5
	4	2.5
	4	2.8
	5	6.0
	4	2.7
	5	...[b]
	4	2.8
	6	...[b]
	4	2.9
	5	...[b]
	4	3.7
	4	2.9
	5	5.6
	4	...[c]
	5	6.0
	5	6.3
	5	6.0
	5	7.0[d]
	5	6.0[d]
	5	6.0
	5	7.0
	5	6.3

Structure	Ring size	$J_{vinyl\ protons}$ (c.p.s.)
	5	6.0[e]
	5	6.0[e]
	5	6.0[e]
	5	5.9[e]
	5	5.58[f]
	5	5.4[g]
	6	10.3
	6	9.9
	6	10.3
	6	10.2
	6	10.2
	6	10.0
	6	10.5
	6	10.0
	6	10.0
	6	10.5
	6	10.0
	6	10.0
	6	10.1
	6	10.0

Structure	Ring Size	$J_{vinyl\ protons}$ (c.p.s.)
	6	10.0
	7	10.3[h]
	7	10.0[h]
	7	9.9
	7	9.7
	7	12.2
	7	12.5
	8	11.8[i]
	8	12.8
	8	12.6[i]

[a] Maximum probable error ±0.5 c.p.s. [b] This coupling constant was not evaluated because of the complexity of the spectrum. [c] The cyclobutene protons were insufficiently resolved for analysis. [d] W. Herz, A. R. de Vivar, J. Romo and N. Viswanathan, *J. Am. Chem. Soc.*, **85**, 19 (1963). [e] R. W. King and P. E. Butler, Abstracts of the American Chemical Society National Meeting, Atlantic City, N. J., September 9–14, 1962, p. 84Q; private communication from Dr. R. W. King. [f] See ref. 11. [g] See ref. 12. [h] Both *cis*-disubstituted double bonds show the same coupling constant. [i] F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962). [j] The coupling constant given is for the conjugated double bond.

lower than the observed values for acyclic olefins.[2,4–7] We have found that the absolute magnitude of the vinyl proton coupling constant in *cis*-cyclic olefins is not constant as predicted but depends strongly on the size of the ring.

Table I summarizes the variation with ring size of the vinyl coupling constant of *cis*-cyclic olefins. Table II presents the data on which Table I is based. Spectra were analyzed by standard methods.[8] Complex spectra were simplified in certain cases by double resonance techniques before analysis.[9–11]

The absolute magnitude of the vinyl proton coupling constant increases as ring size increases from cyclo-

(4) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 85.

(5) S. Alexander, *J. Chem. Phys.*, **28**, 358 (1958).

(6) H. S. Gutowsky, M. Karplus and D. M. Grant, *ibid.*, **31**, 1278 (1959).

(7) A. A. Bothner-By, C. Naar-Colin and H. Günther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(8) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959.

(9) R. Kaiser, *Rev. Sci. Instr.*, **31**, 963 (1960).

(10) R. Freeman, *Mol. Phys.*, **3**, 435 (1960).

(11) The method used was similar to that used by D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962).

butenes (2.5–3.7 c.p.s.) through cyclopentenes (5.4–7.0 c.p.s.) to cyclohexenes (9–11 c.p.s.) and then appears to level out, cycloheptenes (9–12.5 c.p.s.) and cyclooctenes (11–13 c.p.s.). Extrapolation of the value of the vinyl proton coupling constants for four-, five- and six-membered carbon rings to three-membered rings suggests that cyclopropenes should show very low, almost zero, vinyl proton coupling constants. This expectation has been confirmed recently for 3,3-dimethylcyclopropene by Laszlo and Schleyer.[12]

It has been pointed out recently that coupling constants are affected by the nature of substituents in the immediate vicinity.[13] The close agreement in vinyl coupling constant in compounds of the same ring size with varying substituents rules out electronegativity effects as the origin of the observed effect.

The observation that the magnitude of the vinyl proton coupling constant is dependent on ring size should find important use in the determination of structure, although the origin of the effect is far from clear. The changing geometry and strain in the smaller rings, particularly as they are reflected in altered orbital hybridization of the trigonal carbon atoms, must contribute to the ring size effect.

Acknowledgment.—The author wishes to thank Professor E. Wenkert, Professor C. H. DePuy and Dr. R. W. King for nuclear magnetic resonance spectra and stimulating discussion. This investigation was supported in part by a research grant from the Alfred P. Sloan Foundation.

(12) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2017 (1963).
(13) K. L. Williamson, *ibid.*, **85**, 516 (1963).
(14) Alfred P. Sloan Foundation Fellow.

DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY OF
SCIENCE AND TECHNOLOGY
AMES, IOWA

O. L. CHAPMAN[14]

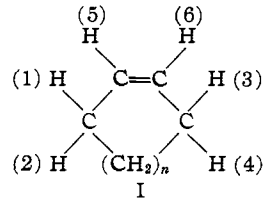
RECEIVED APRIL 10, 1963

N.m.r. Coupling Constants and Conformations of Cycloölefins

Sir:

Correlation of n.m.r. coupling constants (J) with dihedral angles (ϕ) is a major step in conformational and configurational analysis. The familiar Karplus equations[1] are applicable to saturated hydrocarbons, and progress has been made on a similar correlation for olefins.[2-5] However, certain J's have been shown to vary with the electronegativities of substituents near one of the coupled protons[6] and one wonders if other factors are also important. We have solved the olefinic proton splitting pattern of unsubstituted cycloolefins and offer fresh evidence; evidence which not only clearly reveals another factor—variation of J_{56} (I) with ring size—but also discloses new data for possible correlations of J_{15} and J_{16} with dihedral angles.

With the aid of an IBM 7090 computer[7] we interpreted the olefinic proton splitting pattern, as shown in Fig. 1 for *cis*-cycloöctene. Rings with 7, 8 and 10 carbons show nearly the same pattern. Those from cyclopentene and cyclohexene are compressed and not so revealing; *e.g.*, their calculated spectra did not agree



I

perfectly with the experimental spectra and it seems clear that some lines are shifted by nearby lines.[8] The spectra of cyclopentene-1-*d* and cyclohexene-1-*d* should unambiguously reveal J_{15} and J_{16} for these. Giving the computer some $\pm J_{13}$'s and $\pm J_{14}$'s slightly smaller than corresponding J_{16}'s[9] resulted in 53-line

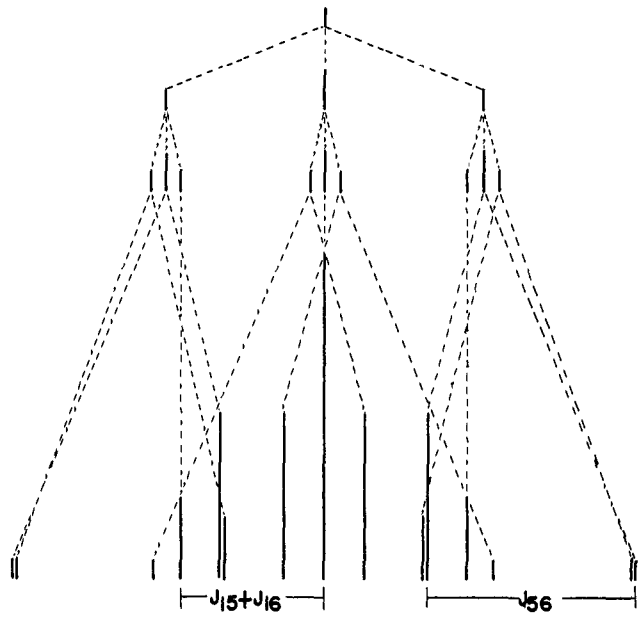


Fig. 1.—Olefinic proton splitting pattern of *cis*-cycloöctene.

spectra. This result causes mainly line broadening of the basic pattern and seems to preclude finding these allylic–allylic proton coupling constants without deuterium substitution.

TABLE I

COUPLING CONSTANTS AND DIHEDRAL ANGLES OF SOME CYCLOOLEFINS

	J_{56}[a] (c.p.s.)	J_{15}[a] (c.p.s.)	J_{16}[a] (c.p.s.)	ϕ_{15},[b] deg.	ϕ_{25},[b] deg.
Cyclopropene	...	1.8[c]	...	66	66
Cyclobutene	(4.0)[d]	(1.5)[e]	(−1.5)[e]	68	68
Cyclopentene	5.1	2.1	−1.4	63	63
Cyclohexene	8.8	3.1	−1.4	43[f]	77[f]
Cycloheptene	10.8	5.7	−1.0	11	109
cis-Cycloöctene	10.3	7.8	−0.8	15	135
cis-Cyclononene	10.7[g]	8.2[g]	− .7[g]	37[h]	157[h]
cis-Cyclodecene[i]	10.8	7.8	− .8	15	135
trans-Cyclodecene[i]	15.1	6.8	− .8	1	121

[a] Probable errors are ±0.1 to ±0.2 c.p.s. See text for discussion of errors in cyclohexene and cyclopentene. [b] Calculated by ignoring probable influence of ring size on J_{15}; see text. [c] Reference 13, p. 1228. [d] "High Resolution NMR Spectra Catalog" Varian Associates, Palo Alto, California, 1962, spectrum 22 of 1,1-dioxathietene; we appreciate Dr. A. A. Bothner-By bringing this to our attention. [e] Estimated from an empirical extrapolation of our data; see also *d*. [f] Assuming $\phi_{12} = 120°$; it may be larger. [g] Dr. A. A. Bothner-By, private communication, has informed us that Mr. Kreiter at Munich has analyzed this splitting pattern and obtains these values. [h] Other probable angles are 27 and 147°. [i] Chemical shifts are for *cis*, 322, and *trans*, 326 c.p.s., from TMS at 60 Mc.; for other shifts, see ref. 13.

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