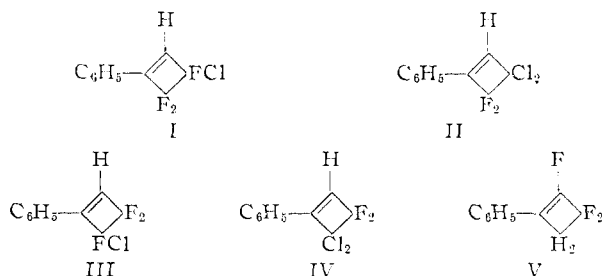


ANOMALOUS SPIN-SPIN SPLITTING IN NUCLEAR
MAGNETIC RESONANCE SPECTRA OF
CYCLOBUTENES¹

Sir:

A spectacular failure of F-F spin-spin coupling constants, A_{ij} , to decrease monotonically with the number of chemical bonds separating nuclei i and j has been deduced from the nuclear magnetic resonance (n.m.r.) spectrum of perfluorodimethylethylamine.² The current importance attached to the use of n.m.r. spectra as a tool for establishment of organic structures prompts us to report a number of similarly anomalous H-F spin-spin coupling constants in cyclobutene derivatives. The present examples are particularly significant in that many of the compounds investigated are (or are derived from) cyclo-addition products of acetylenes with chlorofluoroethylenes³ and would have been assigned quite plausible but incorrect structures on the basis of their n.m.r. spectra alone. Thus, the splitting of the vinyl hydrogen line of the adduct of phenylacetylene with trifluorochloroethylene into a doublet ($A_{ij} = 8$ c.p.s.) while the corresponding line of the adduct of phenylacetylene and 1,1-difluoro-2,2-dichloroethylene is not split by greater than 1-2 c.p.s. perforce suggests these substances to have structures I and II, respectively, even though chemical evidence³ strongly favors III and IV. The only reasonable alternative is to



have the cross-ring H-F splitting (separation by *four* bonds) be substantially greater than the adjacent H-F splitting (separation by *three* bonds). This behavior has been observed repeatedly and twelve examples are listed in Table I which indicate the cross-ring H-F coupling to range from 8-12 c.p.s. and the adjacent H-F coupling to be less than 1-2 c.p.s. Compound V is particularly significant since the method of synthesis (trifluorochloroethylene with styrene followed by dehydrochlorination) and n.m.r. chemical shift data require the assigned structure to be correct and yet the methylene hydrogen absorption is only split into a doublet (12 c.p.s.) by the fluorine across the ring.

The need for caution in assigning structures on the basis of magnitude of spin-spin coupling constants for unusual cyclic compounds should be obvious.

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(1) This work was supported in part by the Office of Naval Research.

(2) A. Saika and H. S. Gutowsky, *THIS JOURNAL*, **78**, 4818 (1956).

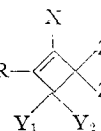
(3) (a) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *ibid.*, **75**, 4765 (1953); (b) J. D. Roberts, *Record of Chemical Progress*, **17**, 95 (1956).

of the substances in Table I, and also to Mr. A. Bottini for discussions and assistance.

TABLE I

CYCLOBUTENE RING PROTON

N.M.R. ABSORPTION^a FOR R-



Compound	R	X	Y ₁	Y ₂	Z	δ^b	Multiplicity	A_{ij} , c.p.s.
IV	C ₆ H ₅	H	Cl	Cl	F	-1.15	..	<1-2
III	C ₆ H ₅	H	F	Cl	F	-1.25	2	8
	C ₆ H ₅	H	F	F	F	-1.30	3	12
c	C ₆ H ₅ ^d	H	Cl	Cl	F	-1.00	..	<1-2
c	C ₆ H ₅ ^d	H	F	Cl	F	-1.15	2	9.4
V ^e	C ₆ H ₅	F	H	H	F	+3.25	2 ^f	12 ^f
c	C ₆ H ₅	Cl	H	H	F	+2.20	..	<1-2
	C ₆ H ₅	Cl	H	Cl	F	-0.28	..	<1-2
c	C ₆ H ₅	H	F	Cl	=O	-1.64	2 ^g	9.2 ^g
c	C ₆ H ₅ ^d	H	F	Cl	=O	-1.83	2 ^g	8.6 ^g
c	C ₆ H ₅	H	F	F	=O	-2.21	3	12.3 ^h
c	C ₆ H ₅	H	=O	F	F	-3.60	..	<1-2

^a Measured using 5-mm. o.d. tubes of pure liquids or solids in 50% acetone solution with Varian Associates High Resolution Spectrometer (V-4300) at 40 mc. and 12-in. magnet equipped with Super Stabilizer. ^b In parts per million, ± 0.06 , referred to water. ^c Preparation to be described in later papers. ^d C₆H₅ is 1-cyclohexenyl. ^e Fluorine spectrum shows triplet vinyl F-absorption, $A_{ij} = 12$ c.p.s. ^f Fluorine spectrum shows doublet with A_{ij} same as for proton.

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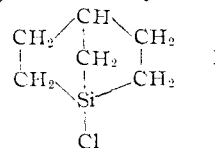
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STEREOCHEMISTRY OF SUBSTITUTION AT A
SILICON ATOM. BRIDGEHEAD ORGANOSILICON
COMPOUNDS¹

Sir:

The elegant syntheses and studies of bridgehead organic halides by Bartlett and co-workers² have played an important part in the elucidation of the stereochemical requirements for substitution at a saturated carbon atom because of the special geometrical situation which exists at a bridgehead atom. This situation effectively prevents back attack and greatly hinders formation of a planar carbonium ion, especially with the bicyclo[2.2.1]-heptyl system,^{2,3} resulting in greatly decreased reactivity toward many reagents.

As a start in the direction of clarifying the stereochemical requirements for substitution at a silicon atom we wish to record the synthesis of 1-chloro-1-silabicyclo[2.2.1]heptane (I) and some preliminary data concerning its reactivity.



(1) Paper 51 in a series on organosilicon chemistry; for 50 see L. H. Sommer, J. M. Masterson, O. W. Steward and R. H. Leitheiser, *THIS JOURNAL*, **78**, 2010 (1956).

(2) P. D. Bartlett and L. H. Knox, *THIS JOURNAL*, **61**, 3184 (1939); P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950).

(3) For recent studies of bridgehead bromides see W. v. E. Doering, M. Levitz, A. Sayigh, M. Sprecher and W. P. Whelan, Jr., *THIS JOURNAL*, **75**, 1008 (1953).