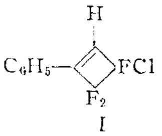
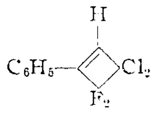
ANOMALOUS SPIN-SPIN SPLITTING IN NUCLEAR MAGNETIC RESONANCE SPECTRA OF CYCLOBUTENES[1]

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 chlorofluoroethylenes[3] 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 evidence[3] 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.


I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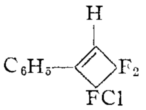
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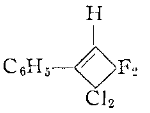
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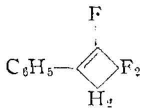
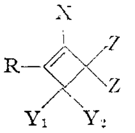

V

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

Acknowledgment.—We are indebted to Drs. Y. Kitahara, R. E. Krall, E. F. Silversmith, E. J. Smutny, and Mr. S. Manatt for samples of many 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_6H_5	H	Cl	Cl	F	−1.15	..	<1–2
III	C_6H_5	H	F	Cl	F	−1.25	2	8
	C_6H_5	H	F	F	F	−1.30	3	12
c	C_6H_9[d]	H	Cl	Cl	F	−1.00	..	<1–2
c	C_6H_9[d]	H	F	Cl	F	−1.15	2	9.4
V[c]	C_6H_5	F	H	H	F	+3.25	2[e]	12[e]
c	C_6H_5	Cl	H	H	F	+2.20	..	<1–2
	C_6H_5	Cl	H	Cl	F	−0.28	..	<1–2
c	C_6H_5	H	F	Cl	=O	−1.64	2[f]	9.2[f]
c	C_6H_9[d]	H	F	Cl	=O	−1.83	2[f]	8.6[f]
c	C_6H_5	H	F	F	=O	−2.21	3	12.3[f]
c	C_6H_5	H	=O		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] C_6H_9 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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[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).

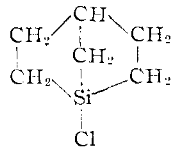
[3] (a) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *ibid.*, **75**, 4765 (1953); (b) J. D. Roberts, *Record of Chemical Progress*, **17**, 95 (1956).

STEREOCHEMISTRY OF SUBSTITUTION AT A SILICON ATOM. BRIDGEHEAD ORGANOSILICON COMPOUNDS[1]

Sir:

The elegant syntheses and studies of bridgehead organic halides by Bartlett and co-workers[2] 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-silabicylo[2.2.1]heptane (I) and some preliminary data concerning its reactivity.


I

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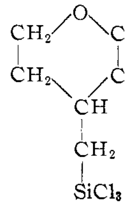
[1] Paper 51 in a series on organosilicon chemistry; for 50 see L. H. Sommer, J. M. Masterson, O. W. Steward and R. H. Leitheiser, THIS JOURNAL, **78**, 2010 (1956).

[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).

The Grignard reagent prepared from 4-bromomethyltetrahydropyran[4] in tetrahydrofuran was added to excess silicon tetrachloride and gave 4-trichlorosilylmethyltetrahydropyran (II), b.p. 63.5° (2 mm.); *Anal.* Calcd. for $C_6H_{11}SiOCl_3$: Si, 12.0; Cl, 45.6. Found: Si, 11.9; Cl, 45.5. Treatment of II with boron trichloride followed by thionyl chloride gave 1,5-dichloro-3-trichlorosilylmethylpentane (III) in 50% yield, b.p. 131° (2 mm.). *Anal.* Calcd. for $C_6H_{11}Cl_5Si$: Si, 9.74; Cl (attached to Si), 36.9. Found: Si, 9.80; Cl (attached to Si), 36.9.



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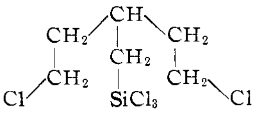

III

Reaction of III with 30% excess magnesium in ether gave a 45% yield of the bridgehead chloride (I), b.p. 54° (5 mm.), n^{20}_D 1.4956. *Anal.* Calcd. for $C_6H_{11}SiCl$: Si, 19.1; Cl, 24.2. Found: Si, 18.8; Cl, 23.9. The infrared spectrum of I showed the absence of Si-H, C=C, and Si-CH_3. Furthermore, the spectrum was rich in detail and contained eight strong and well-defined maxima characteristic of the bicyclic ring system in I which were also present in the two derivatives of I described below.

The bridgehead chloride (I) has an acrid odor, hydrolyzes rapidly in a stream of moist air to give the disiloxane (IV), and undergoes rapid quantitative titration of its Si-Cl bond with 0.1 *N* alkali. The disiloxane (IV), bis-(1-silabicyclo[2.2.1]heptyl) oxide, obtained in 70% yield from treatment of I with wet ether, is a white crystalline solid which sublimes readily and has m.p. 76°. The infrared spectrum, both solution and KBr block, shows the complete absence of Si-OH, has the Si-O-Si maximum at 9.5 μ, and also shows the eight maxima present in I. *Anal.* Calcd. for $C_{12}H_{22}Si_2O$: Si, 23.5; mol. wt., 238. Found: Si, 23.8; mol. wt. (cryoscopically in benzene), 235.

The bridgehead chloride (I) reacted readily with lithium aluminum hydride in ether at 0° and gave a 60% yield of 1-silabicyclo[2.2.1]heptane (V), b.p. 131° (732 mm.), m.p. 63°. *Anal.* Calcd. for $C_6H_{12}Si$: Si, 25.0; H (attached to Si), 0.90; mol. wt., 112. Found: Si, 24.9; H (attached to Si), 0.89; mol. wt., (cryscopically in benzene), 113. The infrared spectrum showed the strong Si-H maximum at 4.65 μ and the eight maxima present in I and IV.

The above facts are in accord with a preliminary working hypothesis which includes the following three postulates: (1) Many nucleophilic displacements on silicon involve formation of an addition complex with the attacking reagent. (2) The geometry of the complex approximates that of a trigonal bipyramid (PCl_5 and PF_5 have this structure in the vapor state)[5] and the bonding is dsp^3. (3) The entering group and the group which is ultimately displaced need not occupy the apices of the trigonal bipyramid. Instead of an angle near 180°, the entering group may form an angle near 90° with the group to be displaced and the central silicon atom.[6]

The high reactivity of I and the mechanism envisaged in the above hypothesis are attributed to the d-orbitals and large size of silicon relative to carbon.

---

[4] A. Burger, L. B. Turnbull and J. G. Dinwiddie, THIS JOURNAL, **72**, 5512 (1950).

[5] For a discussion of the geometry and bonding of PCl_5 and PF_5 see T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, p. 626.

[6] Postulate (1) is at least 30 years old and has been in use up to the present time by chemists working with the organic and inorganic chemistry of silicon. See N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1927, pp. 159-160. Postulate (2) is an attempt to more closely define the geometry of the addition complex in terms of modern theory. Postulate (3) is completely new.

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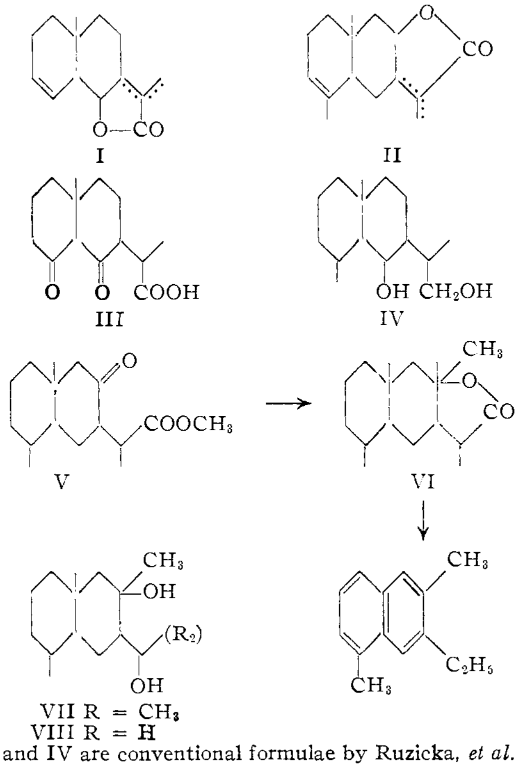
ON THE STRUCTURE OF ALANTOLACTONE

Sir:

Attempts to correlate alantolactone with santonin which belongs to the eudalene group of sesquiterpenes have been entirely unsuccessful.[1-4] Iwai previously has reported the facts: (1) the diketoacid III derived from the 4-ketolactone shows none of the characteristic properties of β-diketones,



III and IV are conventional formulae by Ruzicka, *et al.*

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[1] K. Matsumura, I. Iwai and Ohki, (a) *J. Pharm. Soc. Japan*, **74**, 738 (1954); (b) **74**, 1029 (1954); (c) **74**, 1206 (1954); (d) **74**, 689 (1955).

[2] Mme. C. Asselineau, Mme. S. Bory, and E. Lederer, *Bull. soc. chim. France*, 1524 (1955).

[3] Ö. Kovács, V. Herout, M. Horák, and F. Sorm, *Collection Czechoslov. Chem. Communs.*, **21**, 225 (1956).

[4] L. Ruzicka and J. A. van Melsen, *Helv. Chim. Acta*, **14**, 397 (1931).