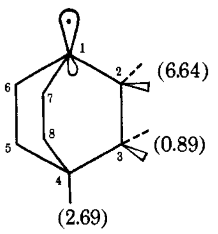
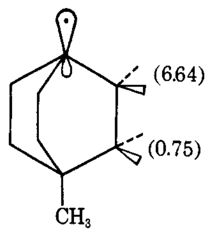
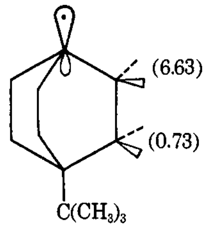


II





Å) but still distinctly pyramidal radicals.[10,11] A more definite statement concerning the relative geometries of the radical sites, however, must await bridgehead ^{13}C-hyperfine coupling data for these radicals (see calculated values in Table I).

The INDO molecular orbital calculations also predict remarkably well the magnitudes of the γ and δ proton hyperfine coupling constants (Table I). The three axial and three equatorial δ protons in the 1-adamantyl radical are strongly differentiated[12] with the largest interaction predicted for the axial protons. Surprisingly, the hyperfine coupling constant of the bicyclooctyl δ proton, situated directly behind the half-filled orbital, not only is smaller in magnitude than the δ-axial hydrogen in I, but also is predicted by the INDO calculations to *decrease* with increased flattening and closer approach of the bridgehead radical center. This casts doubt on the importance of the often involved "backlobe" effect.[1,12] A "through-bond" mechanism[13] for spin delocalization would appear to afford a superior explanation for these observations. In I, the δ-axial C–H bonds and the C$_2$–C$_3$, C$_7$–C$_8$, C$_5$–C$_9$ bonds are all aligned in parallel with the half-filled orbital at C. In II a similar parallel alignment is found with C$_4$–H, C$_2$–C$_3$, C$_7$–C$_8$, C$_5$–C$_6$, and the C$_1$ half-filled orbital. The predicted (INDO) *positive* signs for these long-range coupling constants are also in accord with such a direct mechanism of direct delocalization of spin density.

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[10] Recent calculations by the extended Hückel MO method also predict a pyramidal structure for the 1-adamantyl radical (H. Fujimoto, Y. Kitagawa, H. Hao, and K. Fukui, *Bull. Chem. Soc. Jap.*, **43**, 52 (1970)).

[11] In view of the rather crude geometrical parameterization, no importance is attached to the fact that the structures best fitting the esr data do not correspond to energy minima (*cf.* Table I).

[12] This differentiation, not seen in the 60-MHz nmr spectrum of the 1-adamantyl *cation* (P. v. R. Schleyer, R. C. Fort, Jr., W. E. Watts, G. A. Olah, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **86**, 4195 (1964)), is revealed at 100 and 250 MHz (G. Mateescu, Ph.D. Thesis, Case Western Reserve University, 1971). However, the chemical-shift difference between the δ protons is small.

[13] R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

Orbital Hybridization in Small Fused Rings

Sir:

The marked correlation between hybridization and directly bonded ^{13}C–H spin–spin coupling constants[1-4] has provided the basis for using the coupling parameter to estimate the extent of s character in carbon–hydrogen bonds. The empirical relationships between $J_{\text{C-H}}$ and s_i, the fractional s character in the C–H bond, is given by eq 1, where $K_{\text{C-H}}$ was found to be 500 Hz. The

$$J_{\text{C-H}} = K_{\text{C-H}}s_i \qquad (1)$$

succeeding work of Lynden-Bell and Sheppard[5] and of Frei and Bernstein[6] on ^{13}C enriched compounds extended these hybridizational arguments to directly bonded ^{13}C–^{13}C spin–spin coupling constants, and the relationship which characterizes this dependence on the hybridization of the two directly bonded carbons is

$$J_{\text{C-C}} = K_{\text{C-C}}s_{i(j)}s_{j(i)} \qquad (2)$$

where $s_{i(j)}$ and $s_{j(i)}$ are the fractional s characters at each of the two respective bonded carbon atoms i and j. The second subscript in parentheses designates the second atom in the interacting pair. The constant of proportionality, $K_{\text{C-C}}$, was found[6] to lie in the range 500–575 Hz. While the theoretical work of Pople and Santry[7] and of Maciel, *et al.*,[8,9] indicates that other electronic features affect spin–spin coupling constants, these studies do confirm the importance of hybridizational effects especially in molecules of low polarity such as found in simple hydrocarbons. Weigert and Roberts[10] using a $K_{\text{C-C}} = 550$ Hz exhibited that the s character in cyclopropyl rings is approximately one-sixth in the C–C bonds indicating that p character dominates the carbon–carbon bonding in such small rings. As eq 2 involves two variables $s_{i(j)}$ and $s_{j(i)}$, an additional condition such as symmetry or other independent data must obtain before eq 2 can be applied. Table I contains the experimental $J_{\text{C-C}}$ values obtained on an XL-100-15 Varian spectrometer for a variety of small ring systems. (Note: allene is considered here as a pseudospiro compound for convenience.) The

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[1] M. Karplus and D. M. Grant, *Proc. Nat. Acad. Sci. U. S.*, **45**, 1269 (1959).

[2] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

[3] J. N. Shoolery, *ibid.*, **31**, 1427 (1959).

[4] J. Ranft, *Ann. Phys. (Leipzig)*, **8**, 322 (1961).

[5] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962).

[6] K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).

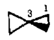
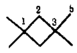
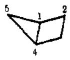
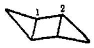
[7] J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

[8] G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 1, 11, 4151, 4497, 4506 (1970).

[9] P. D. Ellis and G. E. Maciel, *ibid.*, **92**, 5829 (1970).

[10] F. J. Weigert and J. D. Roberts, *ibid.*, **89**, 5962 (1967).

Table I

Compd	J_{C-C}, Hz	Restraints on s character	Determined s character
$C^1H_2{=}C^2{=}CH_2$	$J_{12} = 98.7 \pm 0.3$	$s_{2(1)} = 0.5^a$	$s_{1(2)} = 0.36$
	$J_{13} = 20.2 \pm 0.2$	$s_{3(1)} = 0.25^a$	$s_{1(3)} = 0.15$
	$J_{12} = 29.8 \pm 0.2$	$s_{1(2)} = s_{2(1)}^b$	$s_{1(2)} = s_{2(1)} = 0.23$
	$J_{35} = 36.0 \pm 0.2$	$s_{5(3)} = 0.25^c$	$s_{3(5)} = 0.26$
	$J_{12} = 21.0 \pm 0.2$	$s_{2(1)} = 0.15^d$	$s_{1(2)} = 0.25$
	$J_{12} = 36.7 \pm 0.3$	$s_{2(1)} = 0.23^e$	$s_{1(2)} = 0.29$
	$J_{45} = 16.0 \pm 0.2$	$s_{5(4)} = 0.15^d$	$s_{4(5)} = 0.19$
	$J_{23} = 18.2 \pm 0.2$	$s_{3(2)} = 0.15^d$	$s_{2(3)} = 0.22$

[a] Obtained from obvious symmetry arguments, if 100% s character is assumed for all bonds on central carbon. [b] s character assumed to be equal at all carbons within this four-membered ring. [c] sp^3 methyl group assumed. [d] Taken from $s_{2(1)}$ in spiropentane above; also in agreement with one-sixth used by Weigert and Roberts (see ref 10) for cyclopropane. [e] Taken from $s_{1(2)}$ or $s_{2(1)}$ in 1,1,3,3-tetramethylcyclobutane above.

restraint required in either $s_{i(j)}$ or $s_{j(i)}$ for the application of eq 2 is also given. The K_{C-C} = 550 Hz value derived from sp^3–sp^3 hybridization in ethane and used by Weigert and Roberts[10] was adopted in this study. As variations of 10% or more may exist in K_{C-C} depending upon other electronic features, the calculated s values may also exhibit similar errors.

By assuming 0.50 s character in each bond to the central carbon in allene, a hybridization value of 0.36 is obtained from eq 2 for the terminal carbon atoms. Within the limitations of K_{C-C} this value is in excellent agreement with the 0.33 hybridization of an idealized sp^2 terminal carbon atom. Thus, allene corroborates the selection of 550 Hz as a reasonable value for K_{C-C}.

Symmetry arguments may also be applied to the central carbon in spiropentane[11] to establish the s character at 0.25. This yields a value of 0.15 for the hybridization of the peripheral carbons in their bonds with the central carbon atom. Once again, the result reconfirms the hybridization of carbon in three-membered rings.[10]

Two additional assumed relationships are invoked in setting restraints on $s_{i(j)}$ or $s_{j(i)}$ in the case of 1,1,3,3-tetramethylcyclobutane.[12] First, all ring hybridizations within the cyclobutane ring are assumed to be equal, and second, the hybridization of the sp^3 methyl carbon is taken to be 0.25. These lead to hybridizations of 0.23 for the internal ring bonds and 0.26 for the external C–C bond from the cyclic four-membered ring. One may conclude from these results that sp^3 hybridization is appropriate for characterizing the electronic structure of cyclic four-membered rings. It is interesting to note further that the total s hybridization about the quaternary carbon adds up to 0.98 [$2s_{3(2)} + 2s_{3(5)}$], thereby confirming the reasonableness of this admittedly simple treatment. Using the J_{C-H} value of 131.8 Hz at the methylene ring carbon and eq 1, an s character of 0.26 for the carbon part of the C–H bond is also obtained. Again, the total s contribution [$2s_{2(H)} + s_{2(1)} + s_{2(3)}$] = 0.98 about the methylene carbon is compatible with the assumption that the carbon s orbital is completely used for bond formation in this system.

The above considerations provide an approach for evaluation of the hybridization of such fused ring systems as bicyclo[1.1.0]butane,[13] bicyclo[2.1.0]pentane,[14] and *trans*-tricyclo[3.1.0.0^{2,4}]hexane.[15] As indicated in Table I, s = 0.15 was used for all CH$_2$ groups in three-membered rings and s = 0.23 for a CH$_2$ in a four-membered ring. For the case of the bicyclobutane system these values lead to a 0.25 hybridization of the bridgehead carbon to the methylene carbon. Thus, the value is essentially the same as found for cyclobutanes. Using eq 1 and the bridgehead C–H coupling constant of 202 Hz[13] one may fix the s hybridization in this bond at 0.40 which leaves by difference the s character in the bridgehead C–C bond at only 0.10. Thus, the bridgehead C–C bond is constructed primarily from p orbitals and is largely of a π character because of the geometry of the molecule.

A similar treatment of bicyclopentane using the data in Table I, along with a ^{13}C–H coupling at the bridgehead of 178.1 ± 0.5 Hz, indicates that the s orbital contribution available for the C–C bridgehead bond now has risen to 0.16. Thus, the s character which is still significantly below the sp^3 level normally associated with tetravalent carbon atoms has increased to a value comparable with that found in other cyclopropane rings. The general similarity of $s_{2(3)}$ = 0.22 in *trans*-tricyclohexane and $s_{4(5)}$ = 0.19 in bicyclopentane is taken as an indication that carbons at the bridgehead of a fused three–four bicyclic moiety are electronically similar even though considerably different structures are realized in other parts of the molecule.

It is unfortunate that the bridgehead carbons are structurally equivalent in all of the fused ring compounds, thereby preventing direct observation of the bridgehead coupling constant. Carbon-13 enrichment along with a detailed multiplet analysis of the carbon-13 or proton coupled spectra of the general type undertaken by Lynden-Bell and Sheppard[5] would seem to offer the only solutions to the problem if the parent compounds are to be studied. Such work would be of considerable interest, however, in light of the inferred hybridization changes noted in this study

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(11) The sample of spiropentane was kindly provided by Professor D. Applequist, University of Illinois.

(12) H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951). We thank Mr. David Wonnacott for preparing this compound.

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(15) E. L. Allred and J. C. Hinshaw, *J. Amer. Chem. Soc.*, **90**, 6885 (1968).

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Metal Atom Reactions with Fluorocarbons. I. Nonsolvated Fluoroorganic Zinc Compounds

Sir:

A new technique for the direct synthesis of nonsolvated fluoroorganic zinc compounds has been employed in our laboratories. Zinc atoms have been cocondensed with fluoroalkyl iodides on a liquid nitrogen cooled surface in the manner previously described by Skell and coworkers[1] for the study of carbon atoms and some metallic substances.[2] We have found evidence that zinc atoms (by vaporization of zinc from a hot tungsten crucible under vacuum) insert into C–I bonds and that the resultant organometallic compounds have vastly different properties than those generated by normal solution-phase techniques.

Table I. Product Yields from Reactions of Zinc Atoms with Various Fluorinated Substrates[a]

Substrate	Products[f] CF_3H	CF_3CF_3	$CF_2{=}CF_2$[b]	CF_3CFHCF_3	$CF_3CF{=}CF_2$	[g]	F^-	I^-
CF_3I	0.81	1.7	6.6				8	25
$CF_3I(H_2O)$[c]	23	6.6	8.2				8	30
$CF_3I(CHBr_3)$[d]	1.7	0.81	9.1				13	27
$CF_3I((CH_3)_2C{=}O)$[e]	19	7.4	6.7				70	90
$CF_3I((CH_3)_2C{=}CH_2)$[e]	2.5	2.5	1.3			1.7	7	31
$CF_3I((CH_3)_3CHO)$[e]	17	2.5	0.0				90	92
$CF_3I((CF_3)_2C{=}O)$[e]	1.7	3.3	14		0.0		25	*j*
$CF_3CFICF_3(H_2O)$[c]				31	5.8[h]		0	63

[a] Yields based on zinc vaporized and corrected for the fact that only about 60% of the zinc reaches the reaction zone because of a widespread deposition and obstruction by electrode supports. [b] TFE polymer is also formed. [c] Vapor of fluoroalkyl iodide saturated with water vapor. [d] Vapor of fluoroalkyl iodide saturated with bromoform vapor. [e] An 85:15 mixture of iodide-additive. [f] Volatile products were identified by comparison of ir with those published (D. G. Weiblen, *Fluorine Chem.*, **2**, 449 (1954)). Iodide was determined by washing the residue out with dilute acid and then precipitating as silver salt. Fluoride was determined by precipitation as thorium salt. [g] This product was identified by mass spectroscopy and comparison of nmr spectra with that published (R. A. Mitsch, *J. Amer. Chem. Soc.*, **87**, 758 1965)). [h] Most of this product (65%) was formed on residue pyrolysis at *ca.* 100°. Some heptafluoroisopropyl radical dimer (2%) was detected by mass spectroscopy and glpc. [i] Apparently a very small amount of water was present which had a scavenging effect. [j] The residue was hydrolyzed with concentrated nitric acid which destroyed the iodide.

When zinc atoms reacted with CF_3I, a dark grey matrix was formed that decomposed vigorously on warming to *ca.* −80°. Hexafluoroethane and tetrafluoroethylene (TFE) were the only volatile products (*cf.* Table I), while both fluoride and iodide ions and a fluorine and iodine containing polymer remained in the reactor after distillation. Much of the polymer was formed in the vacuum apparatus above the reactor. Pyrolysis of the residue at 100° yielded only trace quantities of the same volatile products. If water was added to the residue (without pyrolysis) trace quantities of fluoroform and TFE were formed. If the CF_3I vapor was saturated with water vapor before deposition, a good yield of fluoroform resulted, but hexafluoroethane and TFE were still formed.

These results indicate that the fluoroorganic zinc compound formed is unstable at well below room temperature and can be hydrolyzed by water while quite cold. Similar and more striking results were found upon the reaction of zinc atoms with heptafluoroisopropyl iodide saturated with water vapor. The hydrolysis product, 2-hydroheptafluoropropane, was formed in large yield compared to hexafluoropropene. Therefore, the organozinc compound was efficiently hydrolyzed at well below room temperature. This observation is interesting in light of the fact that heptafluoroisopropyl zinc iodide formed in solution is very stable and not very easily hydrolyzed.[3] Furthermore, zinc atoms with heptafluoro-*n*-propyl iodide yielded a large amount of hexafluoropropene on warming to only room temperature. This observation also indicates that these nonsolvated organozinc compounds are much more reactive and less stable than those formed in solution.[4]

Fluoroform is an important product when either acetone or pivalaldehyde is used as an additive. The hydrogen uptake by CF_3 must be free radical in nature for the following reasons. Pivalaldehyde is a good hydrogen atom source, but a poor proton source since it has no enolizable hydrogens. Also, with bromoform as additive (possible proton source but poor hydrogen atom source by bond strength considerations) little fluoroform was detected. Note also the low yield of all products when isobutylene, a good radical scavenger, was the additive. These results are consistent with known free-radical decompositions of fluoroorganic zinc compounds.[4] However, with the nonsolvated

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(1) P. S. Skell, L. D. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, 87, 2829 (1965).

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