S is expressed in terms of the roots of the matrix D^+D, which we call d_i; $S = \Pi d_i^{1/2}$. It is convenient to work with the trace of the matrix D^+D; $\mathrm{tr}(D^+D) = \Sigma_i (D^+D)_{ii}$. The trace is simply expressed as the sum of squares of the overlaps of each mapped orbital and its equivalent; $\mathrm{tr}(D^+D) = \Sigma_i d_i = \langle R\phi_i^A|\phi_i^B\rangle^2$. The elements of the R matrix are determined by an iterative maximization of this trace.

The trace is maximized with respect to the angle w_{ab} in the transform $R(a,b)$, in which $R_{aa} = R_{bb} = \cos(w_{ab})$ and $R_{ab} = -R_{ba} = \sin(w_{ab})$ and all other $R_{kl} = \delta_{kl}$. Then the indices a and b are systematically altered in succeeding transformations until the trace converges to its maximum. Details of this numerical procedure will be presented in greater detail elsewhere.

The final values of the roots d_i allow decisions whether a process is allowed. To refer to a familiar example, the thermal opening of cyclobutene to butadiene, we evaluated the roots for the conrotatory and disrotatory modes. The source of the MO's was an ordinary CNDO computation.[6] Nine of the eleven roots corresponded to σ orbitals which were merely reoriented; all these are ≥ 0.99. The remaining roots were related to the π orbitals of butadiene; the conrotatory motion yielded values of 0.63 and 0.63, while the disrotatory motion gave roots of 0.99 and 0.03. Bearing in mind that only an approximate construction of R was attempted, it seems clear that the implications of these calculations, that the disrotatory route is forbidden while the conrotatory route is allowed, are entirely consistent with the well-established behavior of this system.

The application of this method to the thermal opening of 4-methylcyclobutenone (I, with R = Me) is of central interest here. In this case, 11 of the roots corresponded to σ bonds which were merely reoriented, and were indistinguishable from unity whether the *cis* or *trans* ketene was formed. The remaining roots were 0.68, 0.65, 0.81, 0.79, and 0.05 for the thermal formation of the *cis* ketene, and 0.53, 0.89, 0.68, 0.95, and 0.98 for the formation of the *trans* isomer II. The presence of the near-vanishing root for the opening to the *cis* isomer indicates that the process is forbidden; in contrast, the formation of the *trans* ketene is allowed. The conclusions are in accord with the previously established experimental data.[2]

The role of the methyl group (or other 4- substituents) in the opening of cyclobutenones is worth attention in view of the result that *the opening of unsubstituted cyclobutanone is forbidden* according to mapping calculations. It must be assumed that the perturbation on the ring system due to the methyl substituent has the effect of mixing into the ring wave function excited configurations which correlate with the ground state of the ketene. The perturbation is not a strictly repulsive effect which could be ascribed to steric interaction; rather the methyl is attracted to C_3 and repelled from C_2, as shown by the signs of the bond-order matrix. Given this topology of interaction, examination of the signs of the bond order in the ketenes leads to the conclusion that the methyl must be rotated away from the carbonyl group in order that the interactions of the methyl with the remainder of the ketene be of the correct sign. This argument is applicable to both the (+) and (−) optical isomers of methylcyclobutenone, which accounts for Baldwin's recovery of a single *trans* isomer from racemic cyclobutenone. The calculations presented here suggest determination of the relative rates of opening of substituted and unsubstituted cyclobutenones, in order to determine the energetic significance of topological constraints.

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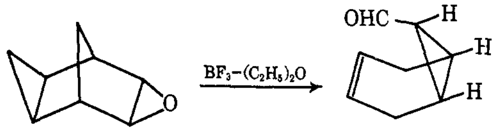
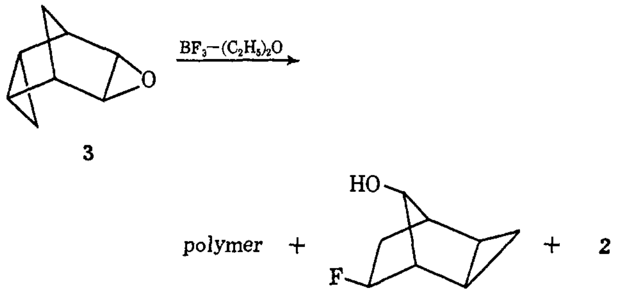
Nucleophilicity of Remote Cyclopropane. The Facile Acid Catalyzed Rearrangement of *exo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene *exo*-Oxide

Sir:

Acid catalysis effects the smooth, rapid conversion of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene *exo*-oxide (**1**) exclusively to *endo*-7-bicyclo[4.1.0]hept-3-enecarboxaldehyde (**2**). This reaction provides an economical, stereospecific entree to the synthesis of *endo*-7-substituted Δ^3-norcarene derivatives. Contrasted with the behavior of *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene *exo*-oxide (**3**), which on treatment with BF_3–$(C_2H_5)_2O$ yields largely polymeric material, this result provides strong support for the suggestion that cyclopropane may function as a nucleophilic neighboring group in this[1,2] and related[3] systems and leads to significant clarification in the structure of the ion which results from such participation. In particular, we are led to infer that cyclopropyl participation in these systems leads to a charge-delocalized ion, which, in the absence of rapid collapse to stable products, can and does isomerize to a charge-localized cation.



1 2



3

(80%) 4 (15%) (5%)

The *exo,exo*-oxide **1** and the *endo,exo*-oxide **3** are obtained in high yield from their respective alkenes[4a] by

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[6] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965); **44**, 3289 1966).

[1] K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965).

[2] A. K. Colter and R. C. Musso, *ibid.*, **30**, 2462 (1965).

[3] P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967).

[4] (a) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964); G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966); (b) K. M. Karach, R. D. Nielsen, and H. W. Rideout, *J. Am. Chem. Soc.*, **82**, 4328 (1960).

treatment with peracetic acid in methylene chloride in the presence of sodium carbonate.[4b] For both compounds, elemental analysis and nmr and infrared spectra are consistent with the structure assigned.

Rearrangement is effected by adding catalytic amounts of BF_3–$(C_2H_5)_2O$ or *p*-toluenesulfonic acid to a stirred solution of epoxide in ether at room temperature. In the case of the *exo,exo*-oxide, a few drops of redistilled commercial BF_3–$(C_2H_5)_2O$ suffice to produce a 50% reduction in peak intensity of two infrared bands (11.5 and 11.9 μ) characteristic of the epoxide 10 min after mixing. Further stirring leads to no additional diminution in peak intensity; however, addition of a few more drops of catalyst does induce further reaction. Apparently the catalyst is in some way consumed as the reaction proceeds, perhaps by complex formation with the product aldehyde. The reaction is continued by adding five–ten drops of catalyst at a time until no further reduction in intensity of the epoxide infrared bands is produced by further addition of catalyst. The nmr spectrum of the reaction mixture taken when 60% or less *exo,exo*-oxide (**1**) has reacted reveals the presence of no product other than aldehyde **2**. Prolonged exposure to BF_3–$(C_2H_5)_2O$ does result in subsequent reaction of the aldehyde.

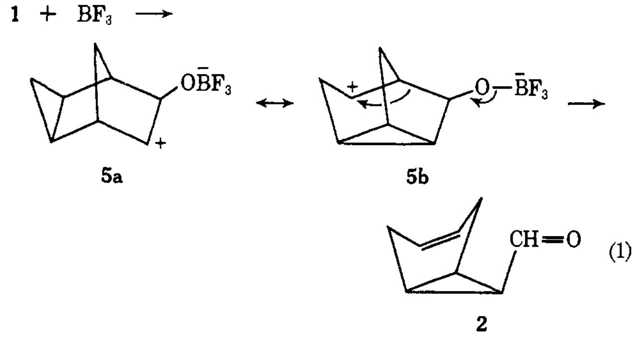
Rearrangement of the *endo,exo*-oxide appears qualitatively to be less rapid and to require greater amounts of catalyst. Even at low percentage conversion, the nmr spectrum of the reaction mixture reveals the presence of signals extraneous to those generated by the two volatile reaction products (**2** and **4**). Typically only *ca.* 20% of the reaction product obtained on workup can be distilled. The distillate consists of a 3:1 mixture of fluorohydrin **4** and aldehyde **2** and perhaps 5% or less of a third component which is not revealed by nmr or vapor phase chromatography, but whose presence is suggested by thin layer chromatography.

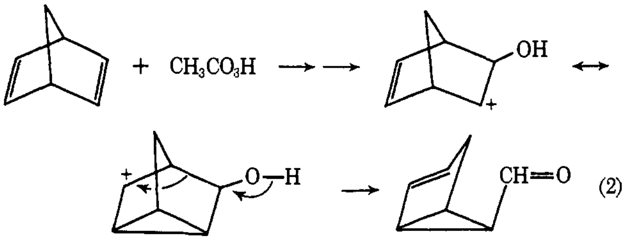
The sole product obtained from rearrangement of the *exo,exo*-oxide gives rise to an nmr spectrum from which its structure may be readily inferred. The spectrum consists of a complex multiplet at τ 0.6 (1 H), a singlet at 4.8 (2 H), a broadened singlet at 7.47 (4 H), and a broadened, poorly resolved doublet at 8.3 (3 H). These signals are assigned to the aldehyde, vinyl, allylic, and cyclopropane protons, respectively, in structure **1**. The coincidental superposition of the signals due to nonidentical cyclopropane protons and the failure of the allylic protons to exhibit marked coupling with vicinal protons are characteristic of this system.[5] A spin-decoupling experiment revealed that the complexity of the aldehydic proton signal stems from long-range coupling with the β-cyclopropane protons; coupling of this type would not be expected if the aldehyde function were substituted *cis* to these protons.[6] The structure inferred from the nmr spectrum was confirmed by oxidation of the aldehyde to the known[5,7] *endo*-7-bicyclo[4.1.0]hept-3-enecarboxylic acid [mp 130–131° (lit. mp 130–131.5,[5] 132°[7]); mmp 130–131°].

The structure of the predominant volatile product derived from reaction of the *endo,exo*-oxide is assigned on the basis of its nmr spectrum. Whereas this spectrum is highly complex, three features permit an unequivocal interpretation. (1) The spectrum includes a high-field (τ 9.0–9.9), four-proton, complex multiplet which can only be attributed to the presence of an *exo*-fused methylene substituent. (2) A broadened singlet ($w_{1/2}$ = 5 Hz) at τ 6.32 can arise only from the proton attached to the carbon bearing the OH substituent whose presence is revealed by the infrared spectrum. (3) A doublet, each portion of which consists of an unresolved multiplet ($w_{1/2}$ = 11 Hz) at τ 5.15, must arise from a proton bound to carbon bearing fluorine ($J_{FH_{gem}}$ = 55 Hz).

The absence of more extensive spin–spin coupling in the signal at τ 6.32 requires that OH and F be nonvicinal[8] and that the OH be placed at C-8.[9] Double irradiation at the frequency for the HCO– proton results in simplification of the signal at τ 5.15. This observation establishes that the HCF and HCO– protons are long-range coupled and thus fixes their mutual orientation as *anti* at the methylene bridge and *endo* at the ethylene bridge.[6,9] Consequently the OH must be *syn* to the fluorine, which must itself be oriented *exo*.

The facile rearrangement of the *exo,exo*-oxide is readily explained by eq 1, which has ample precedent in the sequence of reactions postulated to account for the course of the reaction of norbornadiene with peracetic acid[10] (eq 2). That **5a** and **5b** are truly different canonical forms of the same mesomeric hybrid, and not distinct, isomeric cations, is demonstrated by examining the most probable mechanistic pathway for reaction of the *endo,exo*-oxide (eq 3).





Cations **5** and **6** are identical with respect to the steric disposition of the cyclopropane ring and the electron-deficient carbon. Were **6a** and **6b** distinct, isomeric cations, *i.e.*, were **6b** identical with **7**, one would expect **6** to yield **2** with the same facility as does **5**. If **6b** maintains the geometry implied by the *exo* orientation of the fused cyclopropane ring, however, concerted rearrangement to an aldehyde with conservation of orbital symmetry,[11] in analogy to the collapse of **5**, would

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[5] J. A. Berson and E. S. Hand, *J. Am. Chem. Soc.*, **86**, 1978 (1964).

[6] See, for example, A. Padwa, E. Shefter, and E. Alexander, *ibid.*, **90**, 3717 (1968), and references therein cited.

[7] H. Musso and H. Biethan, *Chem. Ber.*, **97**, 2282 (1964).

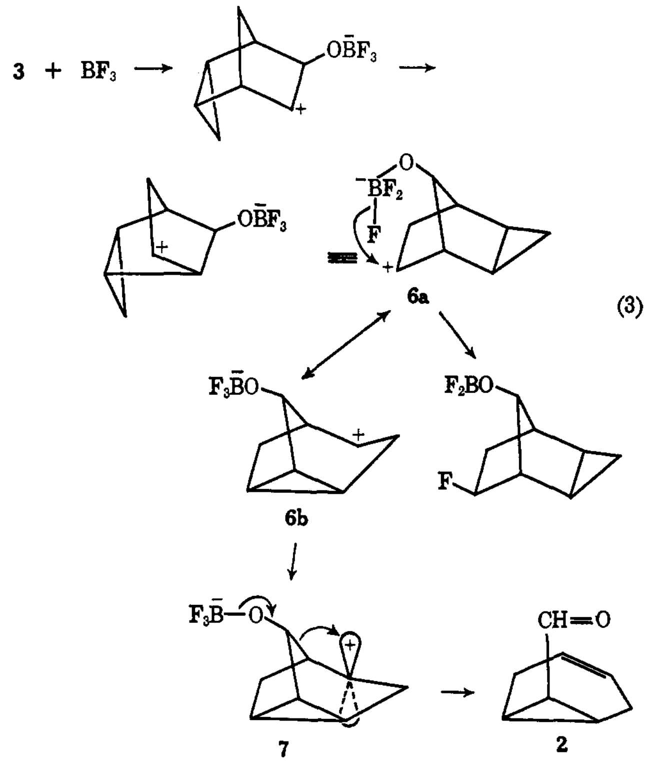
[8] K. L. Williamson and J. C. Fenstermaker, *J. Am. Chem. Soc.*, **90**, 342 (1968).

[9] J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

[10] J. Meinwald, S. S. Labana, and M. S. Chada, *J. Am. Chem. Soc.*, **85**, 582 (1963).

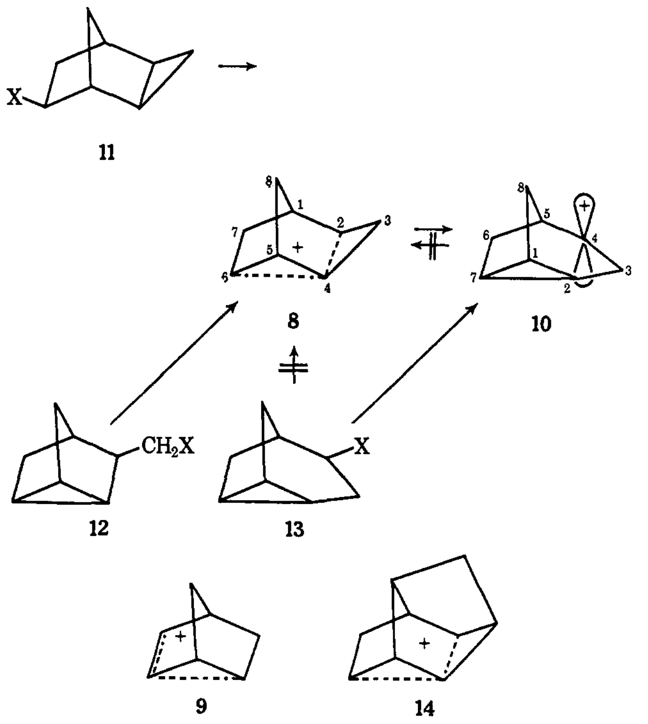
[11] Reviews: R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

lead to an untenable *trans*-fused cyclohexene double bond. The formation of fluorohydrin **4**, generated by a process known to intrude only in the absence of suitable intramolecular pathways for neutralization of positive charge,[12] and the high yield of polymer testify to the inefficiency by which **2** is formed from **6**.



The observation that **2** is formed readily from **5** but sluggishly from **6** is most economically interpreted by inferring that the 6-tricyclo[3.2.1.0^{2,4}]octyl cation is a charge-delocalized intermediate, whose structure permits distribution of the electron deficiency between C-6 and C-2 without formal rupture of the C-2, C-4 σ bond.[13] For this reason this ion might best be represented as **8**, in analogy to the commonly employed representation for the 5-norbornenyl cation (**9**).[15]

This cation (**8**) differs from the charge-localized 4-tricyclo[3.2.1.0^{2,7}]octyl cation (**10**) not only in electronic structure, but also in conformational orientation at C-3. The orientation of C-3 required by **8** is such that this charge-delocalized cation may be generated directly from 6-tricyclo[3.2.1.0^{2,4}]octyl[1,14] (**11**) and nortricyclylcarbinyl[14,16] (**12**) arenesulfonates, but not from 4-tricyclo[3.2.1.0^{2,7}] arenesulfonate[14] **13**, in which severe ground state nonbonded repulsions render the requisite orientation at C-3 untenable. If one postulates that during solvolysis of **11**, **12**, or **13** isomerization of **8** to **10** is kinetically irreversible, and that for the reasons just stated, **10**, not **8**, is the initial intermediate derived from **13**, then **8** is the *sole charge-delocalized* intermediate[17] required to explain the structure and stereochemistry of the products[1,14,16] formed in each of these reactions.[18] It seems likely that a similar cation (**14**) intervenes in the solvolysis of 8-tetracyclo[4.3.0.0^{2,4}0^{3,7}]nonyl *p*-bromobenzenesulfonate.[3]



X = arenesulfonate

The orientation of the cyclopropane ring in **1**, which permits,[19,20] but does not ensure,[21] nucleophilic participation at C-6, combined with the favorable geometry of the tricyclooctyl system,[21] may allow cyclopropane participation to *initiate* rearrangement of **1** to **2**. This possibility is under active investigation.

Acknowledgments. We are pleased to express our gratitude to the National Science Foundation for financial support, to Professor Maitland Jones, Jr. for facilitating mass spectral and 100-MHz nmr analyses, to Dr. Nancy Lowry for executing 60-MHz spin-decoupling experiments, and to Professor Marc S. Silver

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[12] J. R. Bull, *Tetrahedron Lett.*, 5959 (1968), and references therein cited.

[13] The present demonstration that the 4-tricyclo[3.2.1.0^{2,7}]octyl cation can exist in isomeric charge-delocalized (**8**) and charge-localized (*cf.* **7**) forms, which is based upon the stereochemistry of capture by an internal nucleophile, complements the similar conclusion of Berson and coworkers,[14] which was prompted by the stereochemistry of capture by external nucleophiles.

[14] J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Am. Chem. Soc.*, **90**, 3238 (1968).

[15] (a) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950); M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954); J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954). (b) For a discussion of the implications inherent in formulations of this type, see G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

[16] R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

[17] Of course several *charge-localized* cations, such as the nortricyclyl carbonium ion and the hydride shift[14] derived 3-tricyclo[3.2.1.0^{2,7}]octyl and 7-tricyclo[3.2.1]oct-2-enyl cations, are also required intermediates.

[18] Berson and coworkers[14] have previously proposed an elegant mechanistic scheme to explain the complex chemistry exhibited by these solvolysis reactions. The principal and perhaps sole virtue of the alternative offered here would appear to be its simplicity.

[19] H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrop, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

[20] M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967).

[21] G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Lett.*, 2275 (1968).

for valuable comments concerning the interpretation of these results.

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Nuclear Magnetic Resonance Spectroscopy. Long-Range Spin-Spin Couplings Involving Carbon-13[1]

Sir:

Relatively few studies have been reported of spin-spin couplings involving carbon and atoms more than one bond removed. Such couplings can often be seen as ^{13}C satellites in spectra of the other nuclei, but unless the spectra are simple, and even if the "inner" satellites can be detected, specific coupling assignments may not be possible. In such circumstances, specific isotopic enrichment can be of great value.[2] Carbon-fluorine[3] and carbon-phosphorus couplings[4] have been directly observed in the natural-abundance ^{13}C satellites. Internuclear double-resonance experiments utilizing observations of proton spectra have been used to study couplings between carbon and nondirectly bonded phosphorus[5] and nitrogen[6] where the proton spectra are relatively simple. We report here some nonbonded couplings between carbon and other nuclei measured directly from ^{13}C spectra in which the protons are decoupled.

Some couplings involving aromatic carbons are given in Table I. With complete proton decoupling, the ^{13}C spectrum of fluorobenzene consists of four doublets. The signs were determined by partial decoupling techniques and analysis of the second-order proton-decoupled ^{13}C spectra of the difluorobenzenes. The proton-decoupled ^{13}C spectrum of 1-fluoronaphthalene consists of ten doublets arising from carbon-fluorine couplings ranging from 0.8 to 250 Hz, while the ^{13}C spectrum of 2-fluoronaphthalene consists of six doublets and four singlets. Substituent effects on carbon-fluorine coupling in fluorobenzenes have been measured for some 30 compounds and will be discussed in detail elsewhere.

Two-bond, carbon-carbon coupling constants have been observed in molecules in which these couplings would be expected to be large on the basis of carbon-proton couplings in similar bonding situations. The C-1,C-3 coupling in 2-butanone is 15.1 Hz and the C-1, C-3 coupling in propyne is 11.8 Hz.[7] A large, three-bond carbon-carbon coupling of 13.95 Hz in pyridine has no analogy in carbon-proton coupling. The signs of the carbon-carbon coupling constants are unknown.

Table I. Coupling of Carbon to Other Elements in $(C_6H_5)_nX$[a]

X	n	J_{CX}[b]	J_{CCX}[b]	J_{CCCX}[b]	J_{CCCCX}[b]
F	1	−245.3	+21.0	+7.7	+3.3
P	3	12.4	19.55	*c*	0
P^+	4[d]	88.4	10.9	12.8	2.9
Hg	2	1186	88	101.6	17.8
B^-	4	49.5[e]		2.6[e]	
H[f]	1	157.5	+1.0	+7.4	−1.1

[a] Signs refer to reduced coupling constants. [b] In hertz. [c] Three lines with spacings of 6.7, 5.1, and 1.6 Hz are seen for the *meta* and *para* carbons. That 6.7 Hz is correct for this splitting has been kindly verified at 25 MHz in unpublished work by Dr. G. S. Reddy of the Central Research Department, Du Pont. [d] Triphenylmethylphosphonium bromide. [e] Boron-11. [f] F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 2967 (1967).

Two-bond, carbon-metal couplings in organometallic compounds may be correlated by the relationships derived by Karabatsos[2] to correlate carbon-proton couplings with proton-proton couplings.[8,9] Three-bond couplings involving carbon in aliphatic compounds (see Table II) have nearly the same magnitudes as three-bond couplings involving protons,[10] although according to the Karabatsos relations one would expect $J_{CX} = 0.3J_{HX}$. On the other hand, couplings involving carbon in aromatic derivatives correlate rather well with $J_{CX} = 0.4J_{HX}$ for the analogous couplings involving protons in vinyl derivatives, although not quite as quantitatively as the corresponding couplings involving benzene and ethylene derivatives[11] (see Table I).

Table II. Coupling of Carbon to Other Elements in $(C_nH_{2n-1})_mX$[a]

X	m	n	J_{CX}[b]	J_{CCX}[b]	J_{CCCX}[b]
F	1	6	−166.6	+19.9	5.25
P	3	4	−10.9	+11.7	12.5
P^+	4	4	+47.6	−4.3	15.4
Hg	2	4	+656	−26.3	100
Sn	4	2	+307.4 321.5	−23.5	
H[c]	1	2	+125	−4.5	

[a] Signs refer to reduced coupling constants. [b] In hertz. [c] See Lynden-Bell and Sheppard.[7]

Differences in the signs of the one-bond, carbon-phosphorus coupling in phosphines and phosphonium ions have been noted previously,[5b,12] but not explained.

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(1) Supported in part by the National Science Foundation and the Public Health Service, Research Grant GM-11072-07 from the Division of General Medical Sciences.

(2) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Am. Chem. Soc.*, 84, 37 (1962).

(3) N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963); J. Reuben and A. Demiel, *J. Chem. Phys.*, **44**, 2216 (1966).

(4) E. A. Pier in "High Resolution Nuclear Magnetic Resonance Spectroscopy," J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Oxford, 1966, pp 1053-1054.

(5) (a) W. McFarlane, *J. Chem. Soc., A*, 1148 (1967); (b) *Proc. Roy. Soc.* (London), **A306**, 165 (1968).

(6) W. McFarlane, *Mol. Phys.*, **10**, 603 (1966).

(7) Analogies are $J_{CCH} = +26.6$ Hz for acetaldehyde (E. Sackmann and H. Dreeskamp, *Spectrochim. Acta.*, **21**, 2005 (1965)) and $J_{CCH} = +49.4$ Hz in acetylene (R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A296**, 385 (1962)).

(8) G. W. Smith (*J. Chem. Phys.*, **39**, 2031 (1963)) has extended the correlation to two-bond, metal-proton coupling.

(9) F. J. Weigert, M. Winokur, and J. D. Roberts (*J. Am. Chem. Soc.*, **90**, 1566 (1968)) showed that the correlation could be extended to one-bond, metal-carbon coupling in organometallic compounds.

(10) Reference 4, pp 688-689.

(11) See Table I, footnote *f*.

(12) W. McFarlane, *Chem. Commun.*, **58** (1967).