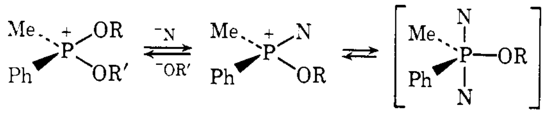
A common feature of any reasonable mechanism which can explain epimerization at phosphorus in the presence of a nucleophile involves bond formation between the nucleophile and the phosphorus atom. Two mechanisms can be advanced involving the formation of a pentacoordinate intermediate (phosphorane). This intermediate, by virtue of its stereochemical nonrigidity, can isomerize[14] prior to re-formation of the phosphonium salt, resulting in epimerization. Alternatively, this phosphorane can react with a second mole of nucleophile to form a hexacoordinate species which may be achiral at phosphorus (trans arrangement of the two nucleophiles). This latter mechanism is difficult to rule out; however, it is important to point out that in one case[17] where nucleophilic substitution at pentacoordinate phosphorus has been observed and postulated to proceed through a hexacoordinate intermediate or transition state, displacement of the equatorial ligands was the preferred pathway. Thus, if the assumption is made that the first addition of a nucleophile to the phosphonium salt occurs in the axial position,[18] the second nucleophile would add to form the octahedral intermediate or transition state of the cis configuration. This species is chiral and would not lead to epimerization at phosphorus without further rearrangements.

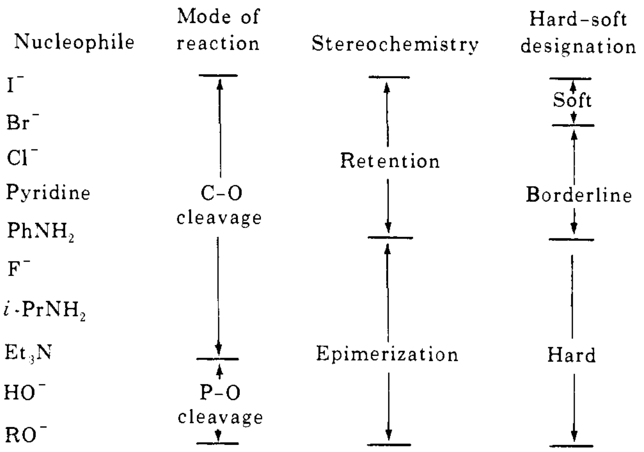
A third mechanism, which has been postulated in similar reactions,[5,19] involving multiple displacements at phosphorus (eq 1), is less likely from our results. It has been observed in the alkaline hydrolysis of $(S)_P$-**1** (displacement at phosphorus) that appreciable (26%) loss of the menthoxy group occurs. Thus in the above system, one would expect crossover to occur in re-formation of the dialkoxyphosphonium salt, leading to dimethoxymethylphenylphosphonium tetrafluoroborate (**3**). The formation of methyl methylphenylphosphinate (**4**) by eventual C–O cleavage of **3** was not detected.



(1)

Our results above have indicated that certain nucleophiles in fact prefer to react at phosphorus rather than at carbon in the dialkoxyphosphonium salt **1** and that this attack is, in certain cases, stereochemically detectable. There appears to be a close analogy between the ability of a nucleophile to induce epimerization at phosphorus and its classification according to the empirical concept of hard and soft acids and bases.[20] Scheme I demonstrates this analogy. Apparently, in the terminology of the HSAB concept, the phosphorus acts as a "hard" acid while the carbon is "soft" or "borderline" in this system. It should be pointed out that our stereochemical probe is not able to detect phosphorane formation of insufficient lifetime to undergo the further transformation necessary to yield epimerized phosphonium salt. Thus, the change in stereochemistry of the displacement reaction as a function of the nucleophile may not directly reflect the change in mode of addition of a nucleophile to the phosphonium salt. We are presently undertaking studies to test the validity of this doubt.

Scheme I



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Kenneth E. DeBruin,* Subramanian Chandrasekaran
Department of Chemistry, Colorado State University
Fort Collins, Colorado 80521

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[13] We have not been able to purify $(R)_P$-**1** to the degree necessary to establish that the 60:40 ratio of $(S)_P$-**2**:$(R)_P$-**2** reflects complete loss of stereospecificity.

[14] Two popular mechanisms for this process are Berry pseudorotation[15] and turnstile rotation.[16]

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Evidence for a Steric Effect on Directly Bonded Carbon–Fluorine and Carbon–Proton Nuclear Magnetic Resonance Couplings[1]

Sir:

Systematic investigations of the proton nmr spectra of a number of alkenes, cycloalkenes, and aromatic hydrocarbons have demonstrated that various types of steric distortions affect the magnitudes of proton–proton coupling constants.[2–5] In the case of the cis-vicinal vinylic coupling, $^3J_{HH}$, both experimental results and approximate theoretical treatments[4,5] of all the reasonable types of strain-induced molecular distortions suggest that in-plane C=C—H bond angle changes

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(1) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 15, 1971, Abstract ORGN-110.

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Table I. Summary of Coupling Constant Data^{a}

No.	Compound	$^{1}J_{^{13}\mathrm{C-F}}$^{b}		
1	Fluorobenzene	−244.5		
2	2-Fluoronaphthalene	−244.7		
3	3,3′-Difluorobiphenyl	−245.4	$^{7}J_{\mathrm{F-F}} < 0.2$	
4	4,4′-Difluorobiphenyl	−246.0	$^{9}J_{\mathrm{F-F}} < 0.2$	
5	2-Fluorophenanthrene	−245.4		
6	3-Fluorophenanthrene	−244.3		
7	1-Fluoronaphthalene	−250.7		
8	1-Fluorophenanthrene	−249.0		
9	1,5-Difluoronaphthalene	−250.3^{c}	$^{5}J_{\mathrm{F-F}} = 4.1$	
10	2,2′-Difluorobiphenyl	−249.6^{c}	$^{5}J_{\mathrm{F-F}} = 18.2$	
11	4-Fluorophenanthrene	−252.2		
12	1,8-Difluoronaphthalene	−255.3^{c}	$^{4}J_{\mathrm{F-F}} = +59.0$^{d}	
		$^{1}J_{^{13}\mathrm{C-F}}$^{e}	$^{3}J_{\mathrm{H-H}}$	C=C—C angle, deg
13	Ethylene	+156.2,^{e} +156.4^{f}	trans +19.1,^{e} 19.1^{f} cis +11.7,^{e} 11.5^{f}	122.0 (C-C-H)^{g}
14	*cis*-2-Butene	+153.4 ± 0.3^{h}	+10.88,^{i} 10.9^{h}	125.0^{j}
15	*trans*-2-Butene	+148.7 ± 0.3^{h}	+15.09,^{i} 15.1^{h}	
16	*cis*-Di-*tert*-butylethylene	+150.4^{h}	+14.2^{h}	136.1^{k}
17	*trans*-Di-*tert*-butylethylene	+149.4^{h}	+16.10^{h}	
18	Cyclobutene	+170.0^{l}	+2.85^{l}	94.3^{m}
19	Cyclopentene	+161.6^{h}	+5.57^{h}	111.5^{n}
20	Cyclohexene	+158.4^{h}	+10.11^{h}	123.3^{o}
21	Cycloheptene	+156.2^{h}	+11.02^{h}	
22	Cyclooctene	+156.0^{h}	+10.41^{h}	

[a] Coupling constants in Hz. [b] There are slight solvent shifts in the magnitude of $^{1}J_{^{13}\mathrm{C-F}}$; values given here are for 50% in acetone except for the less soluble biphenyls which were studied in 50% pyridine; the phenanthrenes were 15–25% in acetone. [c] Obtained from an ABX analysis; in the case of the satellites of **12** a correction of −12.7 Hz has to be applied to the spacing of 268.0 Hz between the centers of the outer ^{13}C-satellite doublets. [d] Sign of $^{4}J_{\mathrm{F-F}}$ determined relative to $^{1}J_{^{13}\mathrm{C-F}}$ as negative by multiple resonance. [e] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 386 (1962). [f] D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963). [g] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **31**, 400 (1959); H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.*, **80**, 2673 (1958). [h] Measured from vinyl proton ^{13}C satellites when methyl protons decoupled; a small negative correction will need to be applied to $^{1}J_{^{13}\mathrm{C-H}}$ based on second-order effects caused by the unknown magnitude of the ^{13}C–C–H couplings. [i] R. K. Harris and B. R. Howes, *J. Mol. Spectrosc.*, **28**, 191 (1968). [j] T. N. Sarachman, *J. Chem. Phys.*, **49**, 3148 (1968). [k] Estimated from calculations and X-ray determined geometries of *o*-di-*tert*-butyl aromatic molecules; see E. H. Wiebanga and E. Bouwhius, *Tetrahedron*, **25**, 453 (1969). [l] E. A. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2047 (1967). [m] B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Andersen, and G. O. Sorenson, *J. Mol. Struct.*, **3**, 369 (1969). [n] G. W. Rathjens, *J. Chem. Phys.*, **36**, 2401 (1962). [o] L. H. Scharpen, J. E. Wollrab, and D. P. Ames, *ibid.*, **49**, 2368 (1968).

provide the major contribution. We now wish to report what we believe represents the first data indicating how $^{1}J_{^{13}\mathrm{C-F}}$ is sensitive to steric effects. For comparison we summarize some $^{1}J_{^{13}\mathrm{C-H}}$ data for simple olefins indicative of steric C=C—H bond angle changes[6] and hybridization changes. Based on semiempirical, theoretical treatments,[7,8] the degree of distortion in the C=C—H bond angle in closely related pairs of molecules has been estimated.

For a number of fluorobenzenes and other fluoroaromatic molecules we recently reported[9] values of $^{1}J_{^{13}\mathrm{C-F}}$. Table I summarizes some of these data and other new data for some cases where we believe no significant resonance, inductive, or possibly hyperconjugative substituent effect modifies the environment of the carbon–fluorine bonds of interest. In **1**, **2**, **3**, **4**, **5**, and **6** the values of $^{1}J_{^{13}\mathrm{C-F}}$ are nearly the same while in **7**, **8**, **9**, and **10** this coupling is some 3–5 Hz more negative, in **11** it is about 7 Hz more negative (−252.2), and in **12** it is about 10 Hz more negative (−255.3 Hz). We propose that these exaltations of $^{1}J_{^{13}\mathrm{C-F}}$ observed in **7–12** all arise from geometrical distortions which are mostly due to significant in-plane bending in the relevant C=C—F bond angles. Assuming a planar carbon atom framework, the peri H–F and F–F distances are 2.43 and 2.42 Å, respectively, and the 4,5-phenanthric H–F and F–F distances are 1.61 and 1.41 Å, respectively. All these distances are less than the sums of the respective van der Waals radii,[10] *i.e.*, 2.6 and 2.8 Å, so significant dispersion forces should be operative.

Recently in a semiempirical treatment of ^{13}C–H and ^{13}C–^{13}C contact couplings, the following formula was suggested

$$J_{^{13}\mathrm{C-X}}\ (\mathrm{X} = \mathrm{H}, {}^{13}\mathrm{C}) = \frac{A a_{\mathrm{C}}{}^{2} a_{\mathrm{X}}{}^{2}}{1 + S_{\mathrm{C-X}}{}^{2}} + B \qquad (1)$$

where A and B are constants, $a_{\mathrm{C}}{}^{2}$ and $a_{\mathrm{X}}{}^{2}$ are the per cent s character of the respective σ-bonding orbitals, and $S_{\mathrm{C-X}}$ is the corresponding overlap integral.[8] For $^{1}J_{^{13}\mathrm{C-H}}$ A was found to be about 1079 Hz, $a_{\mathrm{X}}{}^{2} = 1$, and $B = -54.9$ Hz. Based on the relation of hybridization to orbital direction,[11] it can be shown that $a_{\mathrm{C}}{}^{2} = \cot\theta_{12}\cot\theta_{23}$, where θ_{12} and θ_{23} are the relevant C=C—H angles. Allowing the C=C—C angle θ_{13} to

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(6) Previously several examples of steric effects on $^{1}J_{^{13}\mathrm{C-H}}$ in some sterically hindered methanes were reported: K. L. Servis, W. P. Weber, and A. K. Willard, *J. Phys. Chem.*, **74**, 3960 (1970).

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Table II. Predicted Changes in Directly Bonded ^{13}C-H Coupling Constant with Deformation of C-C-H Angle

Deformation, deg	^{13}C-H^a (aromatic)	^{13}C-H^b (olefinic)
+12	−28.4	−44.6
+10	−19.5	−32.5
+8	−12.3	−22.4
+6	−6.9	−14.2
+4	−3.0	−7.8
+2	−0.8	−3.1
0		
−2	−0.8	+1.5
−4	−3.0	+1.5
−6	−6.9	0.0
−8	−12.3	−3.1
−10	−19.5	−7.8
−12	−28.4	−14.2

[a] With C-C-C angle held at 120° and initially sp^2 carbon. [b] Starting with θ_{12} and θ_{23} of 122.0 and 116.0° for ethylene; see footnote *g*, Table I.

remain constant and θ_{12} to change by small increments, the data in Table II were generated neglecting the small changes of overlap with $a_C{}^2$.

On going from **14** to **16**, the $^1J_{^{13}C-H}$ change suggests a C=C—H angle decrease of 8°; *i.e.*, the proton moves away from the geminal *tert*-butyl group in **16**. The increase of $^1J_{^{13}C-H}$ of +0.7 Hz on going from **15** to **17** may indicate C=C—H angle decreases of the order of 0.7 or 5.3° such that again the proton moves away from a geminal *tert*-butyl group. Recently $^1J_{^{13}C-H}$'s in trimethylethylene (**23**) and tri-*tert*-butylethylene (**24**) were reported to be 148.4 and 143.3 Hz, respectively.[12] The value for **23** is only slightly less than that for **15** which may be taken to indicate similar C=C—H angles. Based on the discussion above, the change of $^1J_{^{13}C-H}$ in **24** represents about a 7° decrease in the C=C—H angle from that in **23**. For the cyclic olefins the main effect causing the increase of $^1J_{^{13}C-H}$ in the smaller rings is not steric effects of bulky groups but rehybridization.[8] The trends in deformation of the C=C—H angle predicted here agree qualitatively with what is expected and are of magnitudes which should be detectable by common structure determination methods.

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Stanley L. Manatt,* M. Ashley Cooper[13]
Space Sciences Division, Jet Propulsion Laboratory[14]
Pasadena, California 91103

Clelia W. Mallory, Frank B. Mallory
Department of Chemistry, Bryn Mawr College
Bryn Mawr, Pennsylvania 19010

Received August 21, 1972

Nuclear Magnetic Resonance of Phosphorus Compounds. VII. Evidence for Steric Effects on the ^{31}P–^{77}Se Coupling and ^{31}P Chemical Shifts[1]

Sir:

In connection with an investigation of the question of p_π–d_π bonding involving phosphorus, we have had occasion to synthesize and study the phosphorus nmr spectra of a number of triarylphosphines and triarylphosphine selenides. We wish to report evidence which indicates how the nmr parameters for phosphorus whose local electronic environment is sterically perturbed can deviate from those expected on the basis of observed substituent effect correlations[2] in less crowded molecules.

There are some practical difficulties which deserve mention regarding the ^{31}P spectra of the triarylphosphines and triarylphosphine selenides which we have studied. Direct determination of the ^{31}P chemical shifts of these classes of compounds is not easily accomplished because extensive spin–spin coupling between the protons on the aromatic rings and phosphorus smears the nmr spectrum for the latter over a wide band. The direct observation of the ^{31}P–^{77}Se coupling in the triarylphosphine selenides, which is exhibited by only 7.5% of the molecules, appeared even more difficult to observe. In addition, many of these compounds possess limited solubility so an increase in concentration was not a possible solution to the signal-to-noise problem. However, taking advantage of proton-noise decoupling[3] along with digital-sweep time averaging[4] and elevated probe temperature, it was possible to make successful measurement of the relevant nmr parameters. Typical spectra are shown in Figure 1.

In the para-substituted triphenylphosphines and phosphine selenides, ^{31}P-chemical shifts correlate linearly with the electronegativity of the substituents[2] with full complement of electrons (*i.e.*, other than H–), but in the case of the *o*-methyl derivatives, we have found substantially upfield ^{31}P chemical shifts as illustrated in Figure 1 and summarized in Table I. The electronic effect of *o*-methyl as a part of the aromatic substituent is not expected to be much different from that of *p*-methyl unless steric factors are important.[5] As appears to be the case for ^{13}C chemical shifts,[6] these

Table I. Phosphorus-31 Chemical Shifts and ^{31}P-^{77}Se Couplings for Some Triphenylphosphines and Phosphine Selenides^a

Substituent on aryl ring	R_3PSe J_{P-Se}, Hz	R_3PSe δ, ppm	R_3P δ, ppm
p-Cl	752.8	+2.21	+3.11
H	735.4	0.00	0.00
p-CH$_3$	723.5	+1.61	+2.47
p-OCH$_3$	719.3	+3.82	+4.61
o-CH$_3$	708.0	+7.57	+24.62
m-CH$_3$	726.3	−0.16	−0.19

[a] $\delta(Ph_3P) - \delta(Ph_3P{=}Se) = 43.02$ ppm.

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[1] Previous paper in this series: A. H. Cowley, J. R. Schweiger, and S. L. Manatt, *Chem. Commun.*, 1491 (1970).

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[4] The system for ^{31}P which was used is a modification of that described previously: M. A. Cooper, H. Weber, and S. L. Manatt, *J. Amer. Chem. Soc.*, **93**, 2369 (1971).

[5] See, for example, R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1966; P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, 70, 841 (1958); and J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965).

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