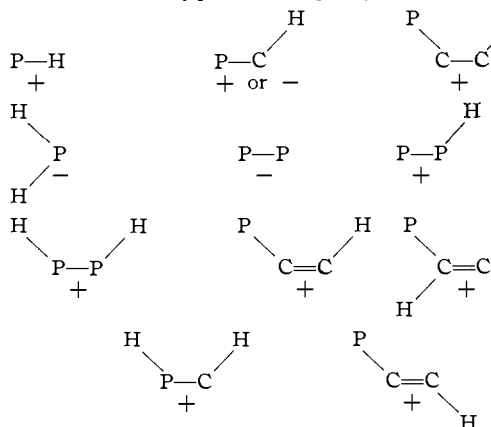


plicated spectrum of this molecule is currently being investigated.

The major contributions to the H-C-C-H, H-P-C-H, and H-P-P-H couplings are expected to be similar and thus these couplings should be of the same sign. The observed magnitudes for these couplings appear to be about the same. The sign of the H-C-C-H coupling has been shown to be positive by relation to the sign of the C¹³-H coupling.^{3,4} Taking the H-P-C-H and H-P-P-H couplings as positive and reasoning from this approach, the P³¹-H coupling is positive.

Based on the data in Table I and the qualitative discussion presented above a correlation of the absolute signs of the various types of couplings can be made.



Acknowledgments.—We are indebted to Dr. Murray Geller for several discussions concerning the theoretical magnitudes of the various contributions to spin-spin coupling. We wish to thank George M. Whitesides, Jesse L. Beauchamp, and Professor John D. Roberts of the Division of Chemistry and Chemical Engineering, California Institute of Technology, for making their results available to us prior to publication.

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Relative Signs of the ³¹P-¹H and ³¹P-C-¹H Nuclear Magnetic Resonance Coupling Constants¹

Sir:

The possibility that terms other than Fermi contact interaction make significant contributions to nuclear spin-spin coupling with heavy nuclei has stimulated considerable interest in the n.m.r. spectra of compounds containing heteroatoms. In particular, relative signs and magnitudes of J_{XCH} and J_{XCCH} have been reported for ethyl derivatives of several heavy isotopes of spin $1/2$.² In order to understand better the factors responsible for spin coupling with a representative heavy nucleus, we have analyzed the spectra of (CH₃)₃P, (CH₃)₂PH, and (CH₃)PH₂ and have obtained relative signs and magnitudes of J_{PH} and J_{PCH} .

The proton spectrum of methylphosphine (Fig. 1) may be treated as the superposition of an A₃B₂ and an A₃X₂ spectrum, using the method of effective chemical shifts.² Inspection of the spectrum suggests that the methyl region can be separated into a triplet at lower field and a more complicated group of lines at higher field. Association of the triplet with the simpler half of

(1) Supported in part by the Office of Naval Research and the National Science Foundation.

(2) For a summary and references, see G. Klose, *Ann. Physik*, **9**, 262 (1962); P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961).

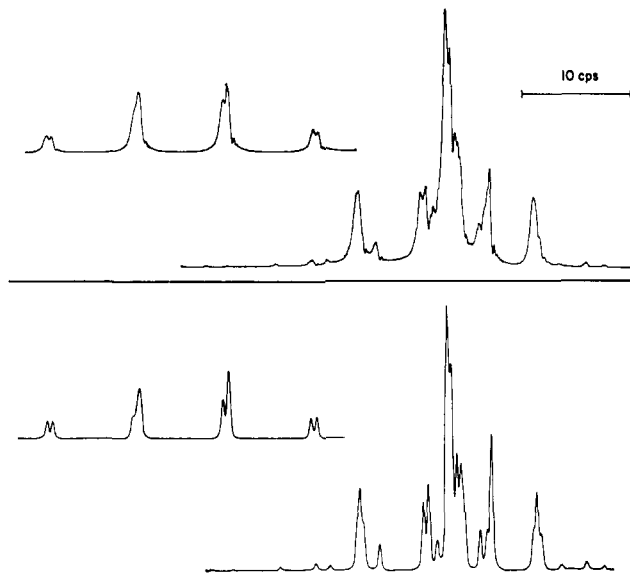


Fig. 1.—Observed (upper) and calculated (lower) proton n.m.r. spectra of methylphosphine at 60 Mc.p.s. The spectral parameters used in the calculated spectrum are given in Table I. The P-H spectrum, also occurring as the lower field part, immediately suggests that J_{PH} and J_{PCH} have the same sign. The spectrum observed for CH₃PH₂ and the spectrum calculated using the parameters in the table are shown in Fig. 1. In both methyl- and dimethylphosphine J_{PH} and J_{PCH} have the same sign; double-resonance experiments performed by Drs. G. Juvinall and S. L. Manatt of the Jet Propulsion Laboratory confirm this conclusion.

TABLE I^a
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR PHOSPHINE DERIVATIVES

Compound	J_{PH}	J_{PCH}	J_{HCPH}	ν_{PH}	ν_{CH_3}
PH ₃ ^b	182.2				
CH ₃ PH ₂	±186.4	±4.1	8.2	157.7	58.5
(CH ₃) ₂ PH	±191.6	±3.6	7.7	187.7	63.8
(CH ₃) ₃ P		2.7			56.3

^a Chemical shifts and coupling constants were moderately temperature dependent; the values reported are for 33°. Chemical shifts are given in c.p.s. at 60 Mc.p.s. from tetramethylsilane as internal standard. ^b R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961).

Anet³ has recently demonstrated by double-resonance experiments that $J^{13}CH$ and J_{HCH} have opposite sign in H₂D¹³COH; Lynden-Bell and Sheppard⁴ have reached the same conclusion for $J^{13}CH$ and $J^{13}CCH$ in H₃-¹³C¹³CH₃ by analysis of the high resolution spectrum.⁴ In contrast, J_{CH} and J_{PCH} have the same sign. Theoretical treatments have indicated that contact interaction will dominate the coupling of directly bonded atoms⁵; more approximate treatments of HCH⁶ and ¹³CCH⁷ lead to the same conclusion.

The observed difference in relative sign of J_{XH} and J_{XCH} for X = ¹H, ¹³C and for X = ³¹P suggests that some mechanism other than the usual σ -bond interactions contribute to spin-spin coupling with phosphorus. Spin-orbital and electron-dipole interaction would be expected to be relatively more important in

(3) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 3767 (1962).

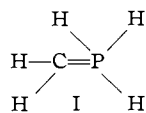
(4) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. (London)*, **A269**, 385 (1962).

(5) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U.S.A.*, **45**, 1269 (1959); N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); J. N. Shoolery, *ibid.*, **31**, 1421 (1959).

(6) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959), and references therein.

(7) G. T. Karabatsos, J. D. Graham, and F. Vane, *J. Phys. Chem.*, **65**, 1657 (1961).

coupling to ^{31}P than to ^1H or ^{13}C due both to the greater anisotropy of the screening around phosphorus⁸ and to the relatively small degree of s-character of its bonding orbitals.⁹ However, Klose has been able to justify the spectrum of $(\text{CH}_3\text{CH}_2)_3\text{P}$ semiquantitatively by a valence-bond treatment using only contact interactions.² Alternately, the d orbitals and nonbonding electrons of phosphorus may be involved in coupling through structures of the "ylene" type (I).¹⁰ Spin-orbital or magnetic-dipole interactions might give



J_{PCH} the observed sign; important contributions from I certainly would. It is not possible to decide which factor is most important on the basis of available experimental evidence.

It is unfortunately not possible to assign an absolute sign to J_{PH} , although such an assignment would be of considerable interest. Recent calculations for several paramagnetic transition metal ions indicate that the contributions of a spin-polarized 3s orbital to the contact term may be opposite in sign to that of a 1s or 2s orbital¹¹; this result suggests that J_{PH} may be either positive or negative, depending upon the relative contributions of the 1s, 2s, and 3s electrons to the coupling.

Acknowledgment.—We are deeply indebted to Dr. F. C. Caserio, Jr., for the phosphine samples used in this research.

(8) J. A. Pople, *Mol. Phys.*, **1**, 216 (1958).

(9) The bond angles in methylphosphine suggest that the phosphorus bonding orbitals in this compound have predominantly p-character: $\angle\text{CPH} = 97^\circ 30'$, $\angle\text{HPH} = 93^\circ 23'$; see E. L. Breig and C. C. Liu, *J. Chem. Phys.*, **35**, 2139 (1961).

(10) This structure is analogous to the hyperconjugative structures used to explain long range coupling in hydrocarbons. Although unimportant in determining the total energy of the molecule, such structures may be very important in spin-spin coupling. See R. A. Hoffman and S. Gronowitz, *Arkiv. Kemi.*, **16**, 471 (1960).

(11) V. Heine, *Phys. Rev.*, **107**, 1002 (1957); R. E. Watson and A. J. Freeman, *ibid.*, **120**, 1125, 1134 (1960).

(12) National Science Foundation Undergraduate Research Participant, 1962.

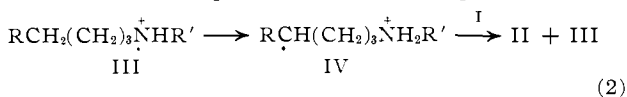
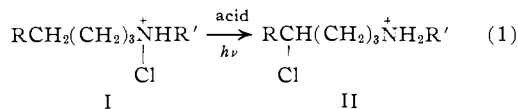
CONTRIBUTION 2967 GEORGE M. WHITESIDES
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RECEIVED JULY 1, 1963

The Chemistry of Ion Radicals. The Free Radical Addition of N-Chlorodialkylamines to Butadiene

Sir:

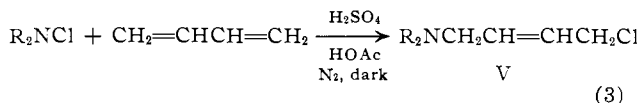
N-Chlorodialkylamines (I) may be rearranged¹ in strongly acidic media under the influence of light, heat, or ferrous ion to the corresponding 4-chloroalkylamines (II) (eq. 1). The sequence $\text{I} \rightarrow \text{II}$ (the Hofmann-Loef-



- a, R = H, R' = n-C₄H₉
b, R = CH₃, R' = n-C₆H₁₁
c, R = C₆H₅, R' = CH₃

(1) A review summarizing the various synthetic applications of this reaction is now available: M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963). However, some of our data, to be reported in the near future, appear to contradict certain of the hypotheses presented therein concerning the optimum conditions and acidity dependence of the photolytic reaction.

fler reaction) proceeds *via* the ion radical III and the alkyl radical IV (eq. 2).^{2,3} However, we have found that the process $\text{III} \rightarrow \text{IV}$ does not take place when N-chloroamines are treated with olefins. In particular, butadiene reacted rapidly (in 15 min.) and spontaneously with Ia-c in acidic media, exclusively *via* the aminium radical III, to afford the 1-chloro-4-dialkylamino-*trans*-2-butenes Va-c (eq. 3) in yields up to 60% (Table I, entries 1, 6, and 7). In each case butadiene was bubbled into a 0.5 M solution of the chloroamine in 4 M sulfuric acid-wet acetic acid under nitrogen at 5–10°; dilution of the reaction mixture with water followed by basification afforded the product. In the presence of oxygen, Va was not obtained from Ia, but instead 72% of dibutylamine and 7% of the neutral products of ionic chlorination, 1-acetoxy-4-chloro-2-butene and 1-chloro-2-acetoxy-3-butene, were isolated. This result and the structure of the adduct V indicated the transformation (eq. 3) to be a free radical chain process. Structure proof of the 1,4-chloroamination products V was based on the infrared and n.m.r. spectra of the amines, elemental analysis of their picrates, and conversion of Va with dibutylamine in benzene to 1,4-bis(dibutylamino)-*trans*-2-butene, also obtained independently from 1,4-dibromo-*trans*-2-butene and dibutylamine.



Even the aminium radical IIIc reacted exclusively by addition to butadiene (Table I, entry 7) in preference to intramolecular hydrogen abstraction ($\text{III} \rightarrow \text{IV}$), although the potential carbon radical IVc was benzylic. Therefore, the free radical 1,4-chloroamination of butadiene by N-chlorodialkylamines *via* the ion radical III is a general reaction representing a useful synthetic route to reactive trifunctional compounds of type V. This process resembles other radical 1,4-additions to butadiene,⁴ but contrasts with the reported⁵ addition of aminium radicals derived from hydroxylamines, followed by coupling, which yielded only 1,8-diamino-octadienes. The presence of the positive charge at the radical center appears to exert no unusual effect upon the course of reaction 3. It is expected, however, that further studies of diene systems now in progress will demonstrate particular effects due to the fully ionic nature of the aminium radical.

Other solvents (Table I, entries 2–5) gave lower yields of the adduct V and increased amounts of the parent dialkylamine. The unprotonated chloroamine (in carbon tetrachloride) failed to undergo any reaction with butadiene, even under strong irradiation (Table I, entry 5). Either the neutral species $\text{R}_2\text{N}\cdot$ was not formed, or it did not add to the diene. Only trifluoroacetic acid (Table I, entries 3 and 8) is a useful alternative solvent to the usual sulfuric acid-acetic acid (Table I, entries 1, 6 and 7), because it can be easily removed under reduced pressure to give the ether-soluble trifluoroacetate salt of the adduct V. In one example (Table I, entry 8) this salt was directly converted with acetic acid-sodium acetate to the acetoxy derivative, thereby

(2) S. Wawzonek and P. J. Thelen, *J. Am. Chem. Soc.*, **72**, 2118 (1950); S. Wawzonek and T. P. Culbertson, *ibid.*, **81**, 3367 (1959).

(3) E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

(4) J. K. Kochi, *ibid.*, **84**, 2785 (1962); A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. H. Hudson, Jr., *ibid.*, **84**, 3897 (1962); M. Asscher and D. Vofsi, *Chem. Ind. (London)*, 209 (1961); S. J. Cristol and K. L. Nagpal, *J. Org. Chem.*, **26**, 365 (1961); F. Minisci and R. Galli, *Tetrahedron Letters*, **No. 12**, 533 (1962).

(5) C. J. Alibisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. F. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).