These arguments can be extended to account for the catalysis of methyl group exchanges in methylthallium systems due to the addition of a vinylthallium species if one assumes that the rate-determining step for exchange involves formation of a bridged species.[6]

(11) NASA Trainee, 1967–1968.

Harry D. Visser,[11] John P. Oliver
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

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The Preparation of Phosphinodifluorophosphine. A High-Yield Synthesis of Difluorophosphine

Sir:

Initial investigations of the reactions of PH_3 with fluorophosphines have shown that, with F_2PI in the presence of mercury, F_2PH is formed in high yield (90%), and that, with a $F_2PI-P_2F_4$ mixture, the new diphosphine H_2PPF_2 is formed along with F_2PH. Only a very small amount of H_2PPF_2 could be detected when pure P_2F_4 was treated with PH_3; the major products were F_2PH and PF_3.[1] The reaction of excess PH_3 with F_2PI gives *no* H_2PPF_2 but only PF_3[1] and a small amount of F_2PH. Apparently, small amounts of H_2PPF_2 are formed according to eq 1, while the scheme given by eq 2 might explain the reaction involving both F_2PI and P_2F_4.

$$PH_3 + P_2F_4 \longrightarrow F_2PPH_2 + F_2PH \qquad (1)$$

$$\begin{array}{l} PH_3 + F_2PI \longrightarrow H_2PPF_2 + HI \qquad (2) \\ \qquad\qquad\qquad\quad \big\downarrow {\scriptstyle P_2F_4} \\ \qquad\qquad\qquad\quad F_2PI + F_2PH \end{array}$$

Phosphinodifluorophosphine, H_2PPF_2, was formed when a mixture of F_2PI (2.17 mmoles) and P_2F_4 (2.00 mmoles) was treated with PH_3 (8.36 mmoles) in a 500-cc bulb, the tip of which was held at −78° for 1 week. Complete separation of the reaction mixture could not be effected by trap-to-trap distillation, but an incomplete separation was obtained by fractional condensation at −130 and −196°. A mixture of F_2PI and H_2PPF_2 was held at −130° while F_2PH, PF_3, and unreacted PH_3 were retained at −196°. Large amounts of phosphinodifluorophosphine could not be obtained free from F_2PI. However, a −112° trap was used to hold the majority of the F_2PI, while 0.84 mmole of H_2PPF_2 (87% pure as demonstrated by a vapor-density molecular weight of 114 g/mole and the ir spectrum) slowly passed through the −112° trap. A pure sample large enough for a mass spectrum (70 eV) was obtained. In the range *m/e* 32–200 the spectrum displayed peaks (relative intensities and assignment in parentheses) at *m/e* 102 (2.0 $H_2PPF_2^+$), 101 (0.3 $HPPF_2^+$), 100 (0.2 PPF_2^+), 88 (25.7 PF_3^+), 70 (13.0 F_2PH^+), 69 (45.2 PF_2^+), 51 (9.2 (FPH^+), 50 (6.2 PF^+), 34.5 (0.2 F_2P^{2+}), 34 (68.8 PH_3^+), 33 (22.9 PH_2^+), and 32 (100.0 PH^+).

The infrared spectrum of gaseous H_2PPF_2 shows absorptions at 2317 (sh, w), 2302 (w), 1065 (br, w), 986 (br, w), 830 (vs), 823 (vs), 727 (m), and 719 (m) in the 4000–650-cm^{-1} region.

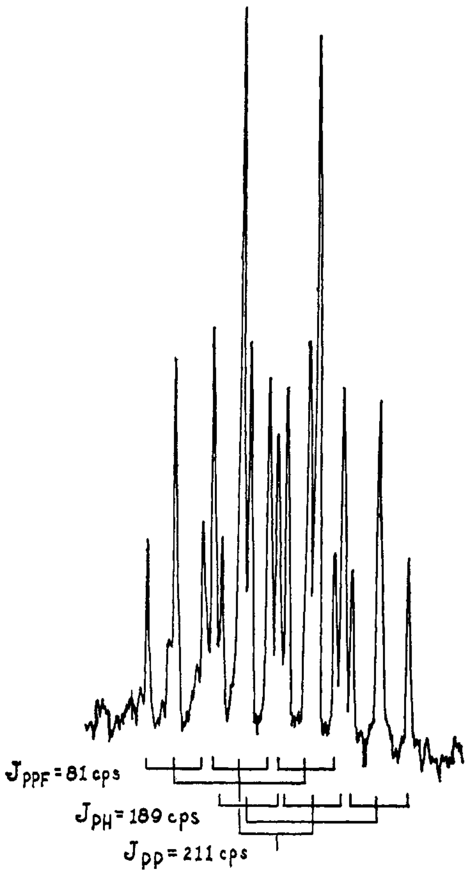

Figure 1. The [$-PH_2$] portion of the ^{31}P nmr spectrum of H_2PPF_2.

Because of the difficulties encountered with purification, analytical and vapor pressure data were not obtained. Nevertheless, unequivocal characterization of phosphinodifluorophosphine was obtained from the ^1H (60 Mc), ^{19}F (94.1 Mc), and ^{31}P (40.5 Mc) nmr spectra.

The proton spectrum at 37° consists of a doublet (J_{PH} = 191 cps) centered −2.75 ± 0.03 ppm from TMS internal standard; each member of the basic doublet displays a doublet of overlapping 1:2:1 triplets (J_{HPPF} = 22, J_{PPH} = 17 cps).

The fluorine spectrum (−40°) displays the same basic pattern as the proton spectrum (doublet of doublets of 1:2:1 triplets) centered +43.2 ± 1.0 ppm from F_2PI internal standard.[2] The coupling constants derived from the ^{19}F spectrum were J_{PF} = 1203, J_{PPF} = 82, and J_{HPPF} = 22 cps.

The phosphorus spectrum (−40°) of H_2PPF_2 gave two signals of equal integrated area, corresponding to the [$-PF_2$] and [$-PH_2$] environments, centered at −51.5 ± 1.0 and +379.8 ± 1.0 ppm from F_2PI internal standard, respectively.[2] The [$-PF_2$] portion of the spectrum consisted of a 1:2:1 triplet of doubled 1:2:1 triplets from which the coupling constants J_{PF} = 1189, J_{PP} = 211, and J_{PPH} = 17 cps were directly measured. As shown in Figure 1, the [$-PH_2$] portion of the spectrum displays a multiplet composed of a basic doublet (J_{PP}

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(1) Disproportionation was evidenced not only by the presence of PF_3 but also by the formation of yellow solids.

(2) F_2PI resonance appears at −31.9 ppm relative to trifluoroacetic acid (TFA) and at −242.2 ppm relative to 85% orthophosphoric acid (OPA): R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, **5**, 1464 (1966). Therefore, the value in the text when stated relative to external TFA is +11.3 ppm; adjusted to external OPA, the values are −293.7 and +137.6 ppm, respectively.

= 211 cps) split into 1:2:1 triplets (J_{PH} = 189 cps) of 1:2:1 triplets (J_{PPF} = 81 cps).

Irrespective of the spectrum from which they were derived, the coupling constants for H_2PPF_2 agree within experimental error, and the magnitude of these *J*'s agrees well with the corresponding values for P_2H_4 and P_2F_4 (Table I). The former values, however, were determined by direct measurement and did not require analysis of second-order spectra as with P_2F_4[3] and P_2H_4.[4] The latter situation is surprising since, rigorously, H_2PPF_2 is an AA'KQXX' spin system, *i.e.*, a system requiring two AX coupling constants AX = A'X', AX' = A'X. A careful examination of the system, however, shows that it would be expected to give "deceptively simple" spectra,[5] *i.e.*, J_{FF} (*gem*) is probably large compared to the couplings between other nonequivalent nuclei[6] and $\delta_{FF'} = 0$. Thus, the observed J_{HPPF} is best explained as an average of two AX couplings.

Table I. The Coupling Constants for H_2PPF_2. A Comparison with Values for P_2F_4 and P_2H_4

	H_2PPF_2				
	^1H	^{19}F	^{31}P	P_2F_4[3]	P_2H_4[4]
J_{PF}	. . .	1203	1189	1198.5	. . .
J_{PH}	191	. . .	189	. . .	186.5
J_{PPF}	. . .	82	81	67.5	. . .
J_{PP}	. . .	. . .	211	227.4	108.2
J_{HPPF}	22	22	. . .	. . .	. . .
J_{PPH}	17	. . .	17	. . .	11.9

Difluorophosphine was originally prepared by the reduction of F_2PI with HI in the presence of mercury.[8] We have since found that, if PH_3 is used instead of HI, the yield of F_2PH is increased from 55 to 90% based on the amount of F_2PI taken.

$$2F_2PI + 2Hg + PH_3 \longrightarrow 2F_2PH + Hg_2I_2 + [PH] \quad (3)$$

The synthesis represented by eq 3 is similar to those described by Harris[9] and Burg and Nixon[10] for the preparation of $(CF_3)_2PH$ and $(CF_3)PH_2$, respectively. Typically, 2.36 mmoles of F_2PI and 3.40 mmoles of PH_3 were added to a 500-cc reaction bulb containing 2 cc of triply distilled mercury. The bulb was then shaken for 15 hr before recovering the desired F_2PH (2.11 mmoles) by fractional condensation at −160°. Unreacted PH_3 (2.34 mmoles) and PF_3 (0.15 mmole) slowly pass through the −160° trap and are retained at −196°.

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R. W. Rudolph
Frank J. Seiler Research Laboratory
Office of Aerospace Research
U. S. Air Force Academy, Colorado 80840

Harvey W. Schiller
Department of Chemistry
U. S. Air Force Academy, Colorado 80840

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(4) R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961); R. Lynden-Bell, *Mol. Phys.*, **6**, 601 (1963).

(5) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961); J. I. Musher, *J. Chem. Phys.*, **36**, 1086 (1962).

(6) We wish to thank Dr. R. Newmark of the University of Colorado for a calculation which showed with $J_{FF'}(gem)$ = 200, *i.e.*, $J_{FF'} \gg J_{HPPF}$, that the spectra of H_2PPF_2 would be "deceptively simple" and appear first order. It should also be noted that one AX coupling constant can be accommodated if a rapidly occurring process of rotation about the P–P bond coupled with inversion through the "phosphino" phosphorus atom is operative. The fact that two vicinal coupling constants are necessary to describe the spectra of P_2F_4[3] and P_2H_4[4] and the fact that calculations have shown the rate of inversion[7] through phosphorus to be slow compared to the nmr constant render this explanation suspect unless some mechanism which lowers the barrier to inversion in H_2PPF_2 is forwarded.

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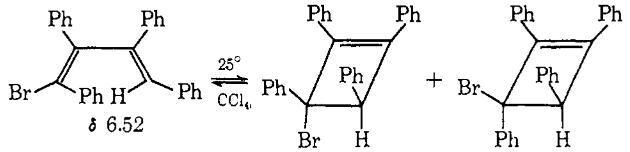
The Facile Thermal Cyclization of a Sterically Hindered Diene

Sir:

Detailed data on the activation parameters for the thermal, electrocyclic ring closure of dienes to cyclobutenes[1] are rare in comparison to that on the kinetically favored reverse process.[2] We now report preliminary details on one of a series of substituted dienes in which steric constraints lead to facile cyclization. In the present instance, diene ring closure is characterized by a $\Delta H^{\ddagger}$ lower than any previously reported for a cyclobutene ring opening.

The diene in question, *trans*-1-bromo-*cis*-1,2,3,4-tetraphenylbutadiene (I),[3] was prepared in 90% yield by the stereoselective 1,4 elimination of HBr from 1,4-dibromo-1,2,3,4-tetraphenyl-*trans*-2-butene[4] at 0°. In CCl_4 solution at 25°, I undergoes a thermal, electrocyclic ring closure which yields both *cis*- and *trans*-3-bromo-1,2,3,4-tetraphenylcyclobutenes (II), the presence of the latter isomer implying a violation of the Woodward–Hoffmann rules.[5] This transformation is accompanied by a decrease in the olefinic proton signal of I and the emergence and growth of two new singlets, the process continuing until equilibrium is established at the values noted.



δ 6.52
I
(26%)

δ 5.22
cis-II
(49%)

δ 4.52
trans-II
(25%)

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(1) The complete kinetics and thermodynamics for the cyclization of two perfluorodienes have been reported: E. W. Schlag and W. B. Peatman, *J. Am. Chem. Soc.*, **86**, 1676 (1964); J. P. Chesick, *ibid.*, **88**, 21 (1966).

(2) H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 183 (1966).

(3) All four possible stereoisomers of the 1-bromo-1,2,3,4-tetraphenylbutadienes have been prepared. Their geometries have been established by halogen–metal exchange with butyllithium followed by protonation (or deuteration) under nonisomerizing conditions (ether, 0°, 5 min). The formation of only the *trans*-1-*d*,*cis*-4-H diene from I uniquely establishes its geometry as shown.

(4) This thermally labile compound has been prepared, without specifying the position or geometry of the double bond, by A. Orechoff, *Ber.*, 47, 89 (1914).

(5) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).