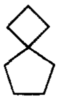
2870, 2850, 1710, 1575, 1400, 1350, 1280, 1190, 1065, 1020, 830, 800, and 765 cm^{-1}; uv (EtOH) λ_{max} 315 (ϵ 51), 228.5 nm (ϵ 11,800); mass spectroscopic mol wt 122. The allylic alcohol **10** could be generated in high yield (90%) by reduction of **9** with diisobutylaluminum hydride at 0–5° in benzene:[7] ^{1}H nmr (CCl$_4$) τ 4.12 (d, d, *J* = 5.6, 1.0 Hz, 1), 4.47 (d, d, *J* = 5.6, 2.0 Hz, 1), 5.39 (m, 1), 6.33 (br s, 1), and 7.60–8.45 (m, 8); ir (neat) 3320, 3040, 2950, 2870, 2850, 1610, 1425, 1355, 1315, 1140, 1070, 1025, 790, and 750 cm^{-1}. The allylic chloride **11** could be prepared in an impure state by heating **10** with a 50% excess of triphenylphosphine in CCl$_4$[8] for *ca.* 1 hr. Nmr analysis of the crude reaction mixture indicated **11** was present as the major component (65–75%): ^{1}H (CCl$_4$) τ 4.02 (d, d, *J* = 5.0, 2.2 Hz), 5.23 (m), and 7.45–8.35 (m). Since the instability of **11** precluded further purification, the crude reaction mixture was utilized in subsequent transformations. The flask containing impure **11** dissolved in dry triglyme and a 100% excess of potassium *tert*-butoxide[9] was connected to a vacuum trap (77°K) and heated to 50° for 1 hr (125 mm). The remainder of the volatile material was removed by heating to 100° (0.07 mm) for 10 min. The volatile hydrocarbon was separated from *tert*-butyl alcohol, solvent, and some other less volatile material by preparative glpc: 6 ft × 0.25 in., SE-30 on 60–80 Chromosorb W, at 65°. The material collected in this manner (30% from **10**) was identified as **2** by its characteristic spectral data: ^{1}H nmr (CCl$_4$) τ 3.65 (m, 2), 3.95 (m, 2), and 7.67–8.07 (m, 6); ir (neat) 3100, 3080, 3060, 3040, 2970, 2940, 2870, 1630, 1510, 1445, 1370, 1330, 1080, 965, 910, 795, 765 (sh), 756, 728, and 715 (sh) cm^{-1}; mass spectroscopic mol wt 106.[10] Catalytic hydrogenation of **2** (PtO$_2$, hexane, 1 atm) resulted in the uptake of 2 mol of hydrogen to produce **12** which was prepared for comparison *via* an alternate and independent route by the Wolff-Kishner reduction of the known ketone **13**.[11] Predictably the diene **2** yielded a 1:1 adduct with maleic anhydride upon standing at room temperature overnight in benzene: mp 91°; ^{1}H nmr (CCl$_4$) τ 3.88 (t, *J* = 2 Hz, 2H), 6.58 (d, d, *J* = 3, 1.5 Hz, 2 H), 6.82 (m, 2 H), and 8.21 (m, 6 H); ir (KBr) 3060, 2980, 2940, 1855, 1775, 1325, 1300, 1220, 1130, 1080, 930, 910, and 660 cm^{-1}. Since orbital interaction is often manifested by an anomalous uv spectrum of the material in question relative to appropriate models, the ultraviolet spectra of **9** and **2** are discussed in some detail. The π–π^* maximum of **9** occurs at 228.5 nm (ϵ 11,800) which is *ca.* 10-nm red shifted relative to 4,4-dimethylcyclopentenone (λ_{max} 218.5 nm (ϵ 12,100)[12] chosen as a model compound. The cause of this shift is difficult to determine due to the distortion caused by the small ring spirocyclic and a lack of more suitable model compounds. However, it should be noted that irradiation of **9** (ether, 0.05 *M*, 3000 Å)[13] leads to the loss of ethylene and production of the dienone **15** (45%).[14] This unusual fragmentation certainly suggests possible interaction between the four-membered ring and the enone moiety in the excited state. The ultraviolet spectrum of **2** shows a similar unusual red shift. In ethanol **2** exhibits a featureless maximum at 261 nm (ϵ 1950) with no other detectable maxima above 210 nm. In comparison with the model compounds **1** (λ_{max} 257 nm (ϵ 2200))[15] and **3** (λ_{max} 254 nm (ϵ 2200)),[15] the spectrum of **2** is significantly bathochromically shifted. While similar ambiguity exists in predicting the effect of geometric distortion, the possibility of direct σ–π interaction in **2** cannot be ruled out. The definitive answer concerning ground-state interactions in **9** and **2** must await analysis by photoelectron spectroscopy which is presently in progress. Investigation of the chemistry of **2** and related derivatives is proceeding.



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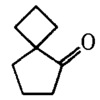

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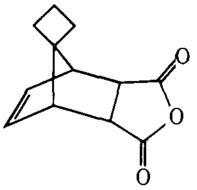

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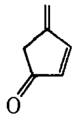

15

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[7] K. E. Wilson, R. T. Seidner, and S. Masamune, *Chem. Commun.*, 213 (1970).

[8] (a) I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind.* (*London*), 900 (1966); (b) J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968).

[9] M. F. Semmelhack, J. S. Foos, and S. Katz, *J. Amer. Chem. Soc.*, **94**, 8637 (1972).

[10] A dimer is formed upon standing at room temperature in carbon tetrachloride: ^{1}H nmr (CCl$_4$) τ 4.46 (m, 3), 4.88 (d, d, *J* = 6, 2 Hz, 1), 6.78 (m, 1), 7.48 (m, 3), and 8.19 (m, 12); mass spectroscopic mol wt 212.

[11] R. Mayer, G. Wenschuh, and W. Topelmann, *Chem. Ber.*, **95**, 1616 (1958).

[12] R. D. Miller, unpublished results.

[13] The irradiation was conducted using a Rayonet Photochemical Reactor (RPR-100) with 3000-Å source lamps.

[14] Spectral data for **15**: ^{1}H nmr (CCl$_4$) τ 2.25 (d, *J* = 5.8 Hz, 1 H), 3.67 (d, d, d, *J* = 5.8, 1.8, 0.9 Hz, 1 H), 4.61 (br s, 1 H), 4.70 (br s, 1 H), and 7.1 (t, *J* = 1.4 Hz, 2 H); ir (neat) 3070 (w), 2980 (w), 2910 (w), 1710, 1635, 1545, 1280, 1175, 935, and 820 cm^{-1}; mass spectroscopic mol wt 94.

[15] C. F. Wilcox, Jr., and R. R. Craig, *J. Amer. Chem. Soc.*, **83**, 4258 (1961).

[16] IBM Postdoctoral Fellow, 1973–1974.

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Received September 15, 1973

Free Radical Reactions of Tetrafluorodiphosphine. The Preparation of 1,2-Bis(difluorophosphino)ethane

Sir:

Initial investigations of the free radical reactions of P$_2$F$_4$[1] have resulted in the preparation of the bidentate ligand, 1,2-bis(difluorophosphino)ethane. F$_2$PCH$_2$-CH$_2$PF$_2$ results in greater than 50% yield from the photochemical reaction of P$_2$F$_4$ (1.9 m*M*) with C$_2$H$_4$ (1.01 m*M*) in the gas phase for a period of 6 hr. The photochemical cell consisted of a 200-ml quartz tube (45-mm o.d.) attached to a vacuum stopcock and a 10/30 joint to allow entry to the vacuum system. A Rayonet photochemical reactor (Southern N. E. Ultraviolet Co., Middleton, Conn.) containing reactor lamps RPR-3000A was used as the energy source. In the

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[1] Evidence has been presented for $\cdot$PF$_2$ in equilibrium with F$_2$PPF$_2$: (a) M. S. Wei, J. H. Current, and J. Gendell, *J. Chem. Phys.*, **52**, 1592 (1970), and (b) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, **88**, 3729 (1966). It has also been suggested that the $\cdot$PF$_2$ radicals have been involved in chemical reactions: (c) K. W. Morse and R. W. Parry, *ibid.*, **89**, 172 (1967), (b) above, (d) G. Bokerman, Ph.D. Thesis, University of Michigan, 1968, and (e) H. W. Schiller and R. W. Rudolph, *Inorg. Chem.*, **50**, 2500 (1971). However, no studies have been reported on the photochemistry of P$_2$F$_4$.

absence of ultraviolet light, the reaction does not proceed. However, at 300° in a sealed tube, P_2F_4 and C_2H_4 give material identical with that obtained in the photochemical reaction. Complete separation of the reaction mixture could be obtained by distillation through traps held at −63, −84, and −196°. Pure $F_2PCH_2CH_2PF_2$ (0.54 m*M*) was retained in the −84° trap only after no more condensable was recovered in the −196° trap. This required distillation periods from 12 to 20 hr. That the sample was pure was demonstrated by the mass spectrum (70 eV) which displayed the following peaks (all observed peaks are assignable to $P_2F_4C_2H_4$) (relative intensities and assignment in parentheses): 166 (15.3 $P_2F_4C_2H_4^+$), 147 (0.88 $FPCH_2CH_2PF_2^+$), 138 (6.32 $P_2F_4^+$ recombination), 97 (16.4 $F_2PCH_2CH_2^+$), 96 (0.70 $F_2PC_2H_3^+$), 83 (1.05 $F_2PCH_2^+$), 78 (1.2 $FPCH_2CH_2^+$), 77 (6.4 $FPC_2H_3^+$), 76 (0.35 $FPC_2H_2^+$), 75 (1.1 FPC_2H^+), 69 (100 PF_2^+), 59 (12.6 $PC_2H_4^+$), 58 (0.46 $PC_2H_3^+$), 57 (4.3 $PC_2H_2^+$), 56 (1.1 PC_2H^+), 55 (0.70 PC_2^+), 51 (4.18 PFH^+ recombination?), 50 (5.72 PF^+), 45 (0.49 PCH_2^+), 44 (0.70 PCH^+), 31 (1.5 P^+), 28 (7.2 $C_2H_4^+$), 27 (2.8 $C_2H_3^+$), 26 (6.0 $C_2H_2^+$).

The vapor density molecular weight also supports the assignment of the formula $P_2F_4C_2H_4$: exptl 171 (calcd 166). The compound is sufficiently stable to obtain vapor pressure data [T(°K), P(mm)]: 252.8, 6.9; 253, 7.85; 273.6, 25.0; 283.0, 41.45; 287.3, 51.75; 299.6, 90.6. The vapor pressure data follow the equation $\log P_{(\mathrm{mm})} = -1776/T + 7.891$. The infrared spectrum of gaseous $P_2F_4C_2H_4$ shows absorptions at 2955 (w), 2910 (m), 2800 (vw), 1645 (vw, br), 1410 (ms), 1197 (ms), 1175 (ms), 1072 (w), 1008 (w), 960 (w), 890 (w), 822 (vvs), 750 (ms), 737 (ms), 708 (s), 472 (m), 469 (ms), 425 (m), 399 (m), and 305–325 cm⁻¹. The infrared spectrum of solid $P_2F_4C_2H_4$ shows absorptions at 2912 (mw), 1420 (w), 1397 (s), 1199 (s), 1181 (s), 1084 (w), 1040 (vvw), 950 (mw), 793 (vvs), 770 (vvs), 720 (mw), 710 (s), 670 (mw), 470 (m), and 305–325 cm⁻¹.

Although analytical data were not obtained, unequivocal characterization of 1,2-bis(difluorophosphino)ethane was obtained from the nmr spectra obtained in the neat liquid.

The proton spectrum (60 MHz) (all spectra reported were run at ambient temperature) consists of a broad singlet centered at +1.6 ppm from TMS (external standard); splitting of the singlet by the other magnetically active nuclei is not distinguishable, and the results of decoupled spectrum will be reported in a succeeding paper.

The fluorine spectrum consists of a 1:1 doublet ($\delta_{\mathrm{CCl_3F}}$ +98.7 ppm) resulting from the splitting of the phosphorus nucleus directly attached to the fluorine (J_{PF} = 1168 Hz).

The phosphorus spectrum displays a sharp 1:2:1 triplet centered −234 ppm from OPA (external standard) corresponding to splitting by two equivalent fluorines directly attached to the phosphorus (J_{PF} = 1170 Hz). No additional splitting of the members of the triplet was discernible.

That $F_2PCH_2CH_2PF_2$ does display dibasic character is reflected by its reaction with diborane. When 0.072 m*M* of $P_2F_4C_2H_4$ and 0.159 m*M* of B_2H_6 were allowed to warm to room temperature together in a reaction vessel, a low volatile colorless liquid formed. Distillation through traps held at 0, −64, and −196° resulted in 0.087 m*M* B_2H_6 being recovered in the −196° trap. Since no volatile was recovered in the 0° trap, mass balance indicates that a 1:1 adduct ($P_2F_4C_2H_4 \cdot B_2H_6$) was recovered in the −64° trap.

The mass spectrum of the low volatile fraction supports the formulation as the borane adduct since peaks were obtained which can be assigned to the $F_2PCH_2CH_2PF_2$ part of the molecule as well as those peaks requiring attachment of boron: *m/e* 193 ($P_2F_4C_2{}^{11}B_2H_9^+$, $P_2F_4C_2{}^{10}B^{11}BH_{10}^+$, $P_2F_4C_2{}^{10}B_2H_8^+$, relative intensity compared to PF_2 as 100 equals 2.5), 45 ($P^{11}BH_3^+$, 8.4), and 44 ($P^{11}BH_2^+$, $P^{10}BH_3^+$, 3.5).

Further evidence for the existence of the adduct is obtained from its nmr spectra.

The proton spectrum consists of a broad 1:1:1:1 quartet centered 0.6 ppm downfield from TMS, J_{BH} = 97 Hz. The methylene protons may be assigned to an unresolved multiplet centered 2.4 ppm downfield from TMS. The fluorine spectrum (ambient temperature) shows a 1:1 doublet (J_{PF} = 1170 Hz) with a chemical shift of +89.3 from $CFCl_3$. The phosphorus spectrum consists of a broadened (compared to $P_2F_4C_2H_4$) 1:2:1 triplet (J_{PF} = 1160 Hz) centered −264 ppm from OPA. The observed splitting is rationalized in the same way as $P_2F_4C_2H_4$, the broadness of the peaks resulting from the expected quadrupolar relaxation by the coordinated boron nucleus, thereby showing that the BH_3 is coordinated to both the PF_2 sites.

The infrared spectrum of solid $P_2F_4C_2H_4 \cdot B_2H_6$ (the peaks in the gas-phase spectrum were very weak because of the low volatility of the sample) shows absorptions at 2975 (w), 2965 (mw), 2919 (m), 2600 (vvw, br), 2422 (s, sh), 2417 (s), 2360 (w), 2230 (vw, br), 1403 (m), 1263 (w), 1250 (w), 1218 (m), 1203 (mw), 1138 (m), 1128 (m), 1100 (mw, br), 1061 (m), 910 (s), 895 (vs), 882 (vvs, sh), 870 (vvs), 786 (vs), 594 (ms), 430 (m), 410 (m), 400 (m), and 360 (s) cm⁻¹.

The sites of BH_3 attachment are also supported by ir evidence since it has been observed that shifts in the PF stretching motions to higher frequencies occur upon coordinate bond formation by the phosphine or by an increase in oxidation state.[2,3] Thus, the increase from ν_{PF} 793 and 770 cm⁻¹ to ν_{PF} 895 and 870 cm⁻¹ for the solid and ν_{PF} 822 to ν_{PF} 892 cm⁻¹ in the gas support that both PF_2 groups have been coordinated.

Acknowledgments. The support of the U. S. Army Research Office—Durham and the Utah State University Research Council is gratefully acknowledged. We are also indebted to Mike Thomas at the University of Utah for some of the ¹⁹F and ³¹P nmr spectra.

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Received July 25, 1973

σ Complex Formation Involving Ambident Phenoxide Ion

Sir:

We wish to report on the unusual interaction between phenoxide ion and 1,3,5-trinitrobenzene (TNB) in dimethyl sulfoxide–methanol medium. Since TNB is