as described above to give the products separated by GLPC, column C, ambient, 150 mL min^{-1}.

The major product (37% yield) proved to be *cis*-2,2-difluoro-1-(1-propenyl)cyclopropane, **3**: IR 740, 937, 1013, 1098, 1225 (s), 1300, 1370, 1470 (s), 1670 (w), 3050 cm^{-1}; NMR δ 5.5–6.1 and 4.65–5.5 (vinyl, complex m, 1 H each), 2.0–2.8 (allylic, complex m, 1 H), 1.7 (CH_3, d, J = 6 Hz, 3 H), 1.6–2.2 and 0.75–1.6 (cyclopropyl CH_2, complex m, 1 H each), ϕ 135.06 (midpoint) (AB, J_{AB} = 155 Hz, $\Delta\nu_{AB}$ = 1237.3 Hz, downfield F is a complex t, J = 13.5 Hz to each cis-H, upfield F is a d of d of d, $J_{F\text{-cis-H}}$ 13.5 Hz, other J = 2, 5 Hz); mass spectrum gave M^+ 118.060 27 ± 0.0022 (18.7 ppm), calcd for $C_6H_8F_2$ 118.0594, dev 0.000 86 (7.3 ppm); other major fragments *m/e* 103 (base), 97, 83, 78, 77, 67, 53, 51, 41, 39; bp 71.5–73 °C.

The minor product (21.9%) was *cis*-2,2-difluoro-3-methyl-1-vinylcyclopropane, **7**: IR 937, 1100, 1130, 1205, 1280 (s), 1477 (s), 1642, 3000 cm^{-1}; NMR (0 °C) δ 5.14–5.59 (vinyl, complex m, 3 H), 2.0–2.4 and 1.59–2.0 (CH, complex multiplets, 1 H each), 1.12 (CH_3, complex m, 3 H); ϕ 138.46 (midpoint) (AB, J_{AB} = 154.55 Hz, $\Delta\nu_{AB}$ = 2463.71 Hz, downfield F, complex t, $J_{F\text{-cis-H}}$ = 14 Hz, upfield F is a br s); mass spectrum gave M^+ 118.0595 ± (4.9 ppm), calcd for $C_6H_8F_2$ 118.0594, dev 0.000 08 (0.7 ppm); other major fragments *m/e* 103 (base), 97, 90, 83, 77, 67, 64, 53, 51, 41, 39

Pyrolysis of *trans*-2,2-Difluoro-1-(1-propenyl)cyclopropane, 2. **2** was pyrolyzed kinetically at 200.65 °C and for preparative purposes at 275 °C for 1 h. The products were separated by GLPC, preparatively on column C at 50 °C to give two products.

The major product (~97% of product) proved to be 3,3-difluoro-5-methylcyclopentene, **10**: IR (gas) ν_{max} 1370 cm^{-1}, also 1627, 1163, 983 cm^{-1}; NMR ($CDCl_3$, 0 °C) δ 6.23 (vinyl, d of d, J = 5.8, 1.5 Hz, 1), 5.81 (vinyl, d of d, J = 5.7, 2 Hz, 1), 2.96 (CH, complex m, 1), 2.83–2.7 (CH_2, complex m, 1), 1.59–2.08 (CH_2, complex d of d, J = 14.2 Hz, 1), 1.35 (CH_3, d, J = 7 Hz, 3); ϕ 83.72 (midpoint) (AB, J_{AB} = 250.82 Hz, $\Delta\nu_{AB}$ = 331.6 Hz, downfield F is a d of t, $J_{F\text{-cis-H}}$ = 17.1 Hz, $J_{F\text{-trans-H}} \simeq J_{F\text{-vinyl}}$ = 5 Hz, upfield F is a (C_5, of d of d, $J_{F\text{-cis-H}}$ = 19.5 hZ, $J_{F\text{-trans-H}}$ = 13.8 Hz, $J_{F\text{-vinyl}}$ = 4.5 Hz); δ 147.6 (C_1, t, $^3J_{C\text{-F}}$ = 10.1 Hz), 126.2 (C_2, d of d, $^2J_{C\text{-F}}$ = 27.2, 28.4, Hz), 133.6 (C_3, t, $^1J_{C\text{-F}}$ = 240.5 Hz), 41.8 (C_4, d of d, $^2J_{C\text{-F}}$ = 22.9, 25.3 Hz), 36.9 (C_5, t, $^3J_{C\text{-F}}$ = 2.5 Hz) 20.4 (C_6, d of d, $^4J_{C\text{-F}}$ = 1.5, 5.1 Hz), mass spectrum gave 118.0595 ± 0.0002 (2.3 ppm), calcd for $C_6H_8F_2$ 118.0594, dev +0.0001 (1.0 ppm).

The minor product (~3% of the product mixture) was 4,4-difluoro-3-methylcyclopentene, **11**: IR (gas) ν_{max} 1160 cm^{-1}; NMR ($CDCl_3$, 0 °C) δ 5.66 (vinyl, complex m, 2), 3.0 (CH, bm, 1), 2.81 (CH_2, t, $J_{H\text{-F}}$ = 15 Hz, 2), 1.06 (CH_3, d of d, J = 2.5, 7.3 Hz); ϕ 101.19 (midpoint), (AB, J_{AB} = 223.8 Hz, $\Delta\nu_{AB}$ = 1159.6 Hz, downfield F is a d of t of t, J = 17, 15, 2.4 Hz, upfield F is a d of t of t, J = 3.5, 15, 2.4 Hz); ^{13}C NMR δ 134.0 (C_2, d of d, $^3J_{C\text{-F}}$ = 2.75, 5.2 Hz), 125.5 (C_1, t, $^3J_{C\text{-F}}$ = 4.88 Hz), 41.31 (C_5, t, $^2J_{C\text{-F}_3}$ = 27.8 Hz), 46.44 (C_3, d of d, $^2J_{C\text{-F}}$ = 24.1 and 27.1 Hz), 12.78 (C_6, d of d, $J_{C\text{-F}}$ = 2.75, 10.3 Hz); mass spectrum gave M^+ 118.0593 ± 0.0008 (7.2 ppm), calcd for $C_6H_8F_2$ 118.0594, dev −0.0001 (0.8 ppm).

The rate (at 200.65 °C) was obtained from the ratio of total products with respect to starting material vs. time. The relative ratio of products did not vary over 5 half-lives. This coupled with the observation of good first-order kinetics over this period indicated that the products were stable under the conditions of the gas-phase pyrolyses. Moreover, to ensure that all products were accounted for, a direct NMR analysis of the product mixture which was condensed directly from pyrolysis vessel into NMR tube indicated that the ratio of products determined thusly was consistent with the GLPC ratio. The mass balance, as determined by this NMR experiment, also was excellent (~95%).

Pyrolysis of *cis*-2,2-Difluoro-1-(1-propenyl)cyclopropane, 3. **3** was pyrolyzed kinetically at 273.65 °C and preparatively at 293.5 °C for 220 min. GLPC separation, preparatively on column C at 30 °C, led to the isolation of four products. *cis*-Piperylene (15%) was identified by comparison of its IR (gas) spectrum with that of an authentic sample. **10** (49%) and **11** (12%) were also identified by comparison of their spectra to those reported above. *cis*-5,5-Difluoro-1,3-hexadiene, **12** (24%), identified as the final product: NMR ($CDCl_3$, 0 °C) δ 5.28–6.23 (vinylic, complex m, 5 H), 1.75 (CH_3, t, J = 18.3 Hz, 3), ϕ 83.7 (complex p, $J_{F\text{-Me}} \simeq J_{F\text{-vinyl H}}$ = 17 Hz); mass spectrum gave M^+ 188 (56% of base peak $(M - CH_3)^+$.

The rate at 273.65 °C was measured as described above, and the integrity of the product mixture was verified by NMR as above, with the mass balance again being high (~93%).

Acknowledgment. We wish to acknowledge with thanks the support of this research in part by the National Science Foundation. We are also grateful to Professor Barry Carpenter for insightful discussions relating to fluorine substituent effects in pericyclic reactions.

Registry No. 1, 694-34-8; **2**, 79517-52-5; **3**, 79517-51-4; **4**, 80997-33-7; **5**, 77613-68-4; **6**, 79517-50-3; **7**, 79517-49-0; **10**, 80997-34-8; **11**, 80997-35-9; **12**, 80997-36-0; 1,3-butadiene, 106-99-0; (*E*)-piperylene, 2004-70-8; (*Z*)-piperylene, 1574-41-0; (trifluoromethyl)phenylmercury, 24925-18-6; Ph_3PCF_2Br·Br, 58201-66-4.

Intramolecular Oxidative Cyclization Reactions of Trivalent Phosphorus and Carbonyl Functions

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Abstract: Phosphonous diesters derived from the reaction of phenylphosphonous dichloride with 2-ketophenols readily undergo head-to-tail intramolecular cyclization in cases where the carbonyl function is an aldehyde, trifluoromethylacetophenone, or diaryl ketone. A methylimine function may also participate in such a reaction. Analogous intermolecular reactions proceed either sluggishly or not at all, indicating the important role of steric and entropy effects. The cyclization yields stable tricyclic phosphoranes; the pentavalent nature of the products was established using NMR techniques. Oxidative cyclization does not occur where the carbonyl group in the phosphonous diester is an ester or a sterically hindered diaryl ketone. A novel solvent and temperature-dependent equilibrium between the trivalent and pentavalent forms of the product derived from phenylphosphonous dichloride and 2-hydroxy-2′,4,4′-trimethoxybenzophenone is reported.

We have previously reported the synthesis of polycyclic phosphoranes by the reactions of salicylaldehyde and 2-hydroxybenzophenone with phenylphosphonous dichloride in the presence of an amine base.[1] Cragg and co-workers have also reported the formation of a tricyclic phosphorane from the base-catalyzed reaction of 2-hydroxyacetophenone and phenylphosphonous dichloride.[2] The structure of the polycyclic phosphoranes is well established in all these cases as a head-to-tail cyclization of a phosphonous diester, **1**. No experimental evidence for the intermediacy of **1** has been reported in any of these cases. Surprisingly, Gopinathan and co-workers[3] have reported that the

(1) Harper, S. D.; Arduengo, A. J. *Tetrahedron Lett.* **1980**, 4331–4334.

(2) Cragg, G. M. L.; Davidowitz, B.; Fazakerley, G. V.; Nassimbeni, L. R.; Haines, R. J. *J. Chem. Soc., Chem. Commun.* **1978**, 510–511.

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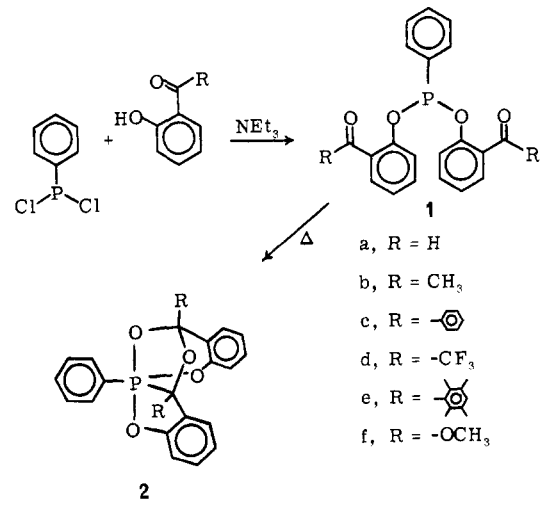

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reaction of the sodium salt of salicylaldehyde with phenylphosphonous dichloride in refluxing benzene yields the phosphonous diester **1a**.

We now report the direct observation of phosphonous diesters **1** as intermediates in the formation of the tricyclic phosphoranes **2**. We also report the first example of an oxidative cyclization at an 8-P-3 center involving an imine function to yield a diazatricyclic phosphorane. The analogous reactions with an α,β-unsaturated function has also been studied.

Results and Discussion

As reported previously, the reaction of salicylaldehyde leads ultimately to the formation of phosphorane **2a** in good yield. At −78 °C in THF the phenylphosphonous dichloride ^{31}P NMR resonance at 160.4 ppm downfield of 85% phosphoric acid immediately gives way to a resonance at 158.3 ppm for the phosphonous diester **1a** on the addition of 2 equiv of salicylaldehyde and tri-*n*-butylamine. At temperatures up to 0 °C the resonance at 158.3 ppm persists with no change. At 0 °C a new resonance at −8.0 ppm upfield of the reference begins to appear and after about 1 h at this temperature the downfield signal is very weak.

The ^{31}P resonance at 158.3 ppm for the diester **1a** is entirely consistent with this structure and similar to that observed for other phosphonous diesters.[4] No other resonances are observed in the course of this cyclization, suggesting that the reaction proceeds cleanly with only short-lived intermediates if any.

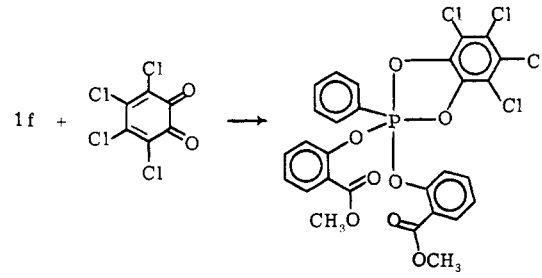
When the cyclization of the phenylphosphonous diester **1a** was followed by proton NMR in CD_2Cl_2, similar results were obtained. Surprisingly, the shift of the aldehyde proton in **1a** was observed to be 10.2 ppm which is substantially different from that reported for the compound isolated by Gopinathan and co-workers.[3] We have been unable to isolate the diester **1a** owing to its ready cyclization to **2a** (the procedure reported by Gopinathan yielded only **2a** in our hands; vide infra). The compound reported by Gopinathan et al. may be an addition complex of salicylaldehyde and phosphorane **2a**.

The esterification to form **1a** at −78 °C is very rapid. NMR spectral studies indicate that the salicylaldehyde is consumed instantly and only resonances for the diester appear. This suggests that the phenylchlorophosphonous monoester reacts rapidly with a second equivalent of salicylaldehyde to form the diester, **1a**.

As we have reported previously, phosphorane **2c** is obtained in high yield from the reaction of 2 equiv of 2-hydroxybenzophenone with phenylphosphonous dichloride.[1] As with phosphorane **2a** we were unable to isolate the intermediate diester **1c** owing to its rapid cyclization to give phosphorane **2c**. If sufficient steric bulk is incorporated in the keto unit, cyclization to the phosphorane can be completely blocked. When 2-hydroxy-2′,3′,5′,6′-tetramethylbenzophenone is allowed to react with phenylphosphonous dichloride, the phosphonous diester **1e** is isolated in good yield.

The diester **1e** resists cyclization to phosphorane **2e** at temperatures as high as 150 °C in THF. The infrared spectrum and ^{13}C NMR chemical shifts indicate that no interaction between the phosphorus and carbonyl occurs. The ^{31}P NMR chemical shift of **1e** (+158.7) is typical of phosphonous diesters.

The cyclization of phosphonous diester of the type **1** can also be blocked by reducing the electrophilicity of the carbonyl group. An ester function would be expected to participate in such reactions less readily. Thus, esterification of phenylphosphonous dichloride with methyl salicylate yields the 8-P-3 species **1f** rather than phosphorane **2f**. This reaction has been reported previously, but the product was not fully characterized.[5] The ^1H NMR spectrum of **1f** displays a singlet at 3.73 ppm due to the methyl esters and a low-field ^{31}P NMR chemical shift of +161.7 ppm consistent with the 8-P-3 structure. The ^{13}C NMR is also consistent with this structure, showing a carbonyl carbon resonance which is similar to that in methyl salicylate.[6] The diester **1f** is stable at temperatures as high as 200 °C in THF, resisting cyclization to **2f**. Reaction of **1f** with tetrachloro-*o*-benzoquinone proceeds smoothly at 25 °C as would be expected to yield phosphorane **3**.



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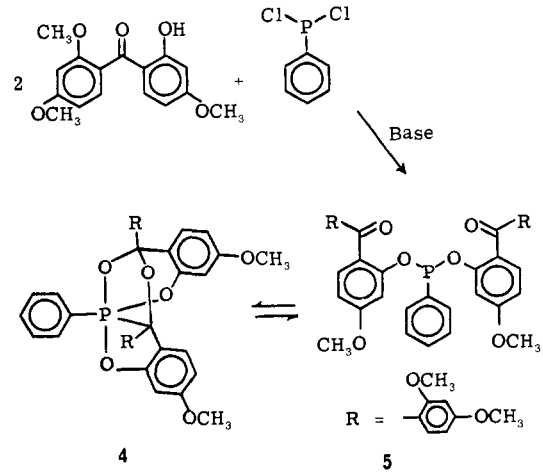
Through the use of both electronic and steric factors we were able to construct a phosphonous diester which undergoes a readily reversible cyclization to a polycyclic phosphorane. The phosphonous diester formed by the reaction of 2-hydroxy-2′,4,4′-trimethoxybenzophenone with phenylphosphonous dichloride undergoes a slow oxidative cyclization at 25 °C in THF to yield phosphorane **5**. After 18 h in THF at this temperature, a weak ^{31}P NMR resonance at +159.7 ppm for the 8-P-3 species is still visible with most of the phosphorus signal observed upfield at −19.5 ppm. Recrystallization of the reaction product from ethyl acetate affords colorless crystals of phosphorane **5**. When **5** is dissolved



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(3) Gopinathan, C., et al. *Indian J. Chem., Sect. A* **1980**, *19*, 596–598.

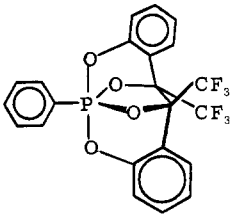
(4) The 8-P-3 species **1a**, **1e**, and **1f** show resonances of +158.3, +158.7, and +161.7 ppm downfield of 85% H_3PO_4. These are similar to the ^{31}P shift of +164.9 reported for the diphenyl ester of phenylphosphonous acid (see Moedritzer, K.; Maier, L.; Groenweghe, L. C. D. *J. Chem. Eng. Data* **1962**, *7*, 307–310).

(5) Vakhidova, V. V.; Mkhamatkhanov, M. M.; Bakhtiyarova, F. A.; Yuldasheva, Kh. E.; Maksudov, N. Kh.; Akbarov, A. *Uzb. Khim. Zh.* **1977**, 66–69.

(6) Scott, K. N. *J. Am. Chem. Soc.* **1972**, *94*, 8564–8568.

in chloroform, the solution begins to develop a deep yellow color and two resonances are observed in the ^{31}P NMR at +160.3 and −18.4 ppm. The downfield resonance initially increases in relative intensity as the solution becomes more yellow. After ~1 h at 25 °C, no further change is observed. The upfield phosphorane resonance is more than twice as intense as the lower field diester resonance. A benzene solution of **5** remains colorless at 25 °C and shows a single phosphorus resonance corresponding to the phosphorane. As the temperature is raised the solution becomes yellow, and the resonance for diester increases in intensity. At 81 °C the relative intensities of the phosphorus signals are about equal. After cooling to 25 °C, the yellow color fades and the diester signal disappears. These observations are consistent with a solvent and temperature-mediated equilibrium between phosphonous diester **4** and phosphorane **5**. A reversible oxidative cyclization of this type has not been previously reported, but equilibria between 8-P-3 and 10-P-5 species have been reported for P–H phosphoranes.[7]

Ramirez has reported the formation of tail-to-tail adducts of α,α,α-trifluoroacetophenone and trivalent phosphorus species.[8] We have found that the reaction of 2-(α,α,α-trifluoroacetyl)phenol with phenylphosphonous dichloride affords the head-to-tail cyclized adduct **2d**. Formation of the isomeric tail-to-tail adduct **6** may



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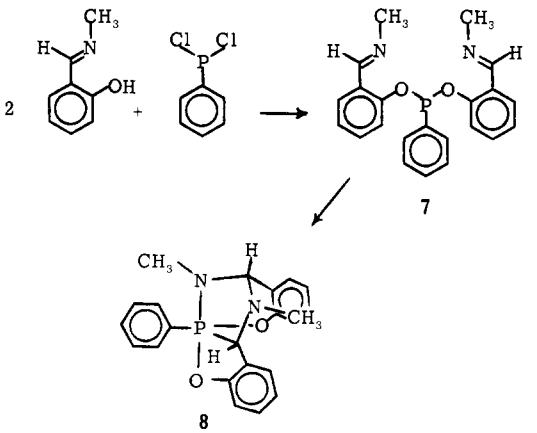
not be favored because of ring strain. The ^{31}P NMR chemical shift of **2d** is similar to that observed for our other head-to-tail cyclicphosphoranes, while the ^{19}F NMR spectrum shows a quartet[9] and a doubtlet of quartets[9] at −80.7 and −76.0 ppm, respectively, for the two nonequivalent trifluoromethyl groups. The ^{13}C NMR is also consistent with this head-to-tail structure.

To further explore the scope of these oxidative cyclizations, we examined the reaction of the methyl imine of salicylaldehyde with phenylphosphonous dichloride. This reaction led cleanly to the phosphorane **8**. We were again unable to isolate **7** because of the



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8

facility of the cyclization forming **8**. Although somewhat sensitive to moisture, the 10-P-5 species, **8**, is a pale yellow crystalline compound which has a ^{31}P NMR shift of −1.7 ppm. The two methine protons appear as doublets in the ^{1}H NMR spectrum at 4.10 and 4.38 ppm. The ^{13}C NMR spectrum provides further information supporting structure **8**. The carbon attached directly to phosphorus appears as a doublet centered at 60.3 ppm with a large (155.3 Hz) phosphorus–carbon coupling constant, while the aminal carbon exhibits a doublet further downfield at 83.6 ppm with a coupling constant of only 8.0 Hz. Similar trends were observed for the salicylaldehyde adduct **2a**. This provides the first example of oxidative cyclization occurring between an 8-P-3 center and imine functions.

Experimental Section

General. Except where noted, all starting materials were purchased from commercial sources and redistilled or recrystallized prior to use. All reactions involving halophosphines were conducted under anhydrous and anaerobic conditions; the glassware was oven-dried, assembled while hot, and repeatedly evacuated and flushed with dry N_2. All solvents were rigorously dried following standard procedures. Melting points are uncorrected. Chemical shifts are reported as parts per million, with positive values indicating the resonance is downfield from fluorotrichloromethane internal reference (for ^{19}F), tetramethylsilane internal reference (for ^{13}C and ^{1}H), or 85% phosphoric acid external reference (for ^{31}P).

3,4:8,9-Dibenzo-1-phenyl-2,6,10,11-tetraoxa-1-phospha(V)tricyclo-[5.3.1.0^{1,5}]undecane (2a). Method A. A solution of 0.68 mL (0.90 g, 0.005 mol) of phenylphosphonous dichloride in 50 mL of THF was added dropwise to a stirred solution of 1.40 mL (1.01 g, 0.01 mol) of triethylamine and 1.07 mL (1.22 g, 0.01 mol) of salicylaldehyde in 125 mL of THF at −78 °C. The cold bath was removed 30 min after the addition was completed and the reaction mixture was warmed to 25 °C. Evaporation to 75 mL gave a solid. The addition of 50 mL of hexane and filtration under N_2 afforded 1.38 g (100%) of triethylamine hydrochloride (identified by ^{1}H NMR).

Evaporation of the filtrate gave a yellow gum which was triturated with 50 mL of ether to yield 1.12 g (64.0%) of phosphorane **2a** as a colorless powder (mp 154–158 °C). An additional 0.17 g (73.7% total) of product was obtained by evaporation of the filtrate to dryness and triturating with 10 mL of ether. The filtrate from the isolation of the second crop consisted primarily of unreacted salicylaldehyde by ^{1}H NMR.

Recrystallization from ethyl acetate yielded **2a** as large colorless prisms: mp 160–163 °C, with decomposition: ^{1}H NMR ($CDCl_3$) δ 5.10 (d, 1 H, J_{PH} = 2 Hz, H1), 6.26 (d, 1 H, J_{PH} = 12 Hz, H3), 6.77–7.67 (m, 11 H, Ar–H), 8.10–8.42 (m, 2 H, H3); ^{13}C NMR ($CDCl_3$) 65.4 (d, J_{PC} = 120.9 Hz, C1), 97.3 (d, J_{PC} = 4.3 Hz, C2) ppm; ^{31}P NMR ($CDCl_3$) −7.9; mass spectrum (70 eV), *m/e* (rel intensity, >20) 350 (M^+, 44), 321 (33), 230 (40), 229 (100), 210 (63), 181 (61), 166 (27), 165 (94), 121 (29), 77 (27), 51 (27), 28 (36).

Anal. Calcd for $C_{20}H_{15}O_4P$: C, 68.57; H, 4.32; P, 8.84. Found: C, 68.41; H, 4.22; P, 8.83.

Phosphorane 2a. Method B. A slurry of 2.88 g (0.02 mol) of salicylaldehyde monosodium salt[10] in 75 mL of THF was cooled to −78 °C, and a solution of 1.36 mL (1.79 g, 0.01 mol) of phenylphosphonous dichloride in 15 mL of THF was added dropwise with stirring. The cold bath was removed 10 min after addition was completed and the reaction mixture warmed slowly to 25 °C. Most of the sodium salt did not react at −78 °C, but dissolved upon warming to 25 °C. After 2 h, nearly all of the initial yellow color of the sodium salt had faded and colorless solids were present. The solution was concentrated to 30 mL under reduced pressure and 20 mL of hexane was added. The precipitated solids were collected by filtration under N_2 through a dry Celite mat. The solids, which contained phosphorane **2a** by ^{1}H NMR, were triturated with 20 mL of chloroform, collected by filtration under N_2, and washed and several small volumes of chloroform. The filtrate was stripped of solvent under reduced pressure to yield a solid residue. Trituration with 20 mL of ether yielded 1.30 (37.1%) of phosphorane **2a** as a colorless powder. The ^{1}H and ^{31}P NMR spectra of the product were identical with those of the phosphorane isolated by method A.

An additional 1.18 g (70.9% total) of phosphorane **2a** was isolated from the original THF/hexane filtrate by stripping off the solvent under reduced pressure and triturating with ether.

Attempted Synthesis of Bis(2-formylphenyl) Phenylphosphonite (1a). A solution of 1.36 mL (1.79 g, 0.01 mol) of phenylphosphonous dichloride in 10 mL of benzene was added dropwise to a stirred suspension of 2.88 g (0.02 mol) of salicylaldehyde monosodium salt in 20 mL of benzene at 25 °C. No reaction was apparent. On warming to reflux the

(7) (a) Bernard, D.; Laurenco, C.; Burgada, R. *J. Organomet. Chem.* **1973**, *47*, 113–123. (b) Burgada, R.; Laurenco, C. *Ibid.* **1974**, *66*, 255–270.

(8) (a) Ramirez, F.; Smith, C. P.; Meyerson, S. *Tetrahedron Lett.* **1966**, 3651–3656. (b) Ramirez, F.; Gulati, A. S.; Smith, C. P. *J. Am. Chem. Soc.* **1967**, *89*, 6283–6288.

(9) There is a rather large J_{FF} = 9.0 Hz in this structure which may be due to the close proximity of the two trifluoromethyl groups. Only one of the trifluoromethyls is observed coupling to P (J_{PF} = 7.0 Hz).

(10) Brady, O. L.; Bodger, W. H. *J. Chem. Soc.* **1932**, 952–957. Elemental analysis (C, H, Na) was in agreement with the empirical formula $C_7H_5O_2Na$.

solution turned clear and nearly colorless. After a few minutes fine colorless solids began to precipitate. After heating at reflux 3 h, the solid (NaCl) was collected by filtration through a dry Celite mat under N_2. The clear yellow filtrate was concentrated in vacuo to yield ca. 10 mL. The colorless crystals which formed on standing were collected by filtration under N_2 following the addition of 10 mL of ether. The solid weighed 2.23 g (63.7%) after drying. The ^1H and ^{31}P NMR spectra of the product, which melted 156.5–161 °C, were identical with those of phosphorane **2a** previously isolated (vide supra). A second crop of phosphorane **2a** weighing 0.41 g (75.4% total) was obtained by stripping the filtrate to dryness and triturating with 10 mL of ether.

3,4:8,9-Dibenzo-1,5,7-triphenyl-2,6,10,11-tetraoxa-1-phospha(V)tricyclo[5.3.1.0^{1,5}]undecane (2c). A solution of 0.63 mL (0.83 g, 0.0046 mol) of phenylphosphonous dichloride in 40 mL of THF was added dropwise to a stirred solution of 1.29 mL (0.93 g, 0.0092 mol) of triethylamine and 1.82 g (0.0092 mol) of 2-hydroxybenzophenone[11] in 240 mL of THF at −78 °C. The cold bath was removed 30 min after addition was completed and the reaction mixture warmed to 25 °C. The solvent volume was reduced to 70 mL in vacuo. The precipitated triethylamine hydrochloride (1.28 g, 100%; identified by ^1H NMR) was collected by filtration under N_2 following the addition of 40 mL of hexane.

The filtrate was stripped of solvent under reduced pressure to yield a yellow gummy residue. Trituration with 50 mL of ether yielded 1.59 g (68.8%) of phosphorane **2c** as a colorless powder (mp 170–172 °C, with decomposition). An additional 0.27 g (80.5% total) of **2c** was obtained by stripping the filtrate to dryness and triturating with 15 mL of ether. The filtrate from the isolation of the second crop contained largely unreacted 2-hydroxybenzophenone as determined by ^1H NMR and TLC.

Recrystallization from ethyl acetate afforded phosphorane **2c** as small colorless crystals: mp 177–178 °C, with decomposition; ^1H NMR ($CDCl_3$) δ 6.53–7.97 (m, Ar–H); ^{31}P NMR ($CDCl_3$) −14.0; mass spectrum (70 eV), *m/e* (rel intensity, >20) 503 ($M^+ + 1$, 33), 502 (M, 100), 321 (48), 305 (44), 181 (64), 152 (27), 105 (44), 77 (53), 28 (22).

Anal. Calcd for $C_{32}H_{23}O_4P$: C, 76.48; H, 4.61; P, 6.17. Found: C, 76.27; H, 4.60; P, 5.89.

Bis(2-durylphenyl) Phenylphosphonite (1e). A solution of 1.36 mL (1.79 g, 0.01 mol) of phenylphosphonous dichloride in 20 mL of THF was added dropwise to a stirred solution of 5.08 g (0.02 mol) of 2-hydroxy-2′,3′,5′,6′-tetramethylbenzophenone[12] and 2.78 mL (2.02 g, 0.02 mol) of triethylamine in 80 mL of THF at −78 °C. The cold bath was removed 30 min after addition was completed and the mixture warmed slowly to 25 °C. The solids were collected by filtration under N_2 following the addition of 20 mL of hexane. The solids weighed 8.09 g and contained triethylamine hydrochloride and another compound exhibiting aromatic resonances and nonequivalent methyl resonances in the ^1H NMR.

The filtrate was stripped of solvent under reduced pressure to yield a small amount of gum which was determined by ^1H NMR to be largely unreacted 2-hydroxy-2′,3′,5′,6′-tetramethylbenzophenone.

The solids were treated with 100 mL of 5:1 water/acetone and stirred vigorously. The solids which remained were collected by filtration, washed with acetone, and dried overnight under high vacuum to yield 5.64 g (91.9%) of phosphonous diester **1e**.

The product was recrystallized from chloroform/ethyl acetate to yield **1e** as fine pale yellow needles: mp 229–231 °C, with decomposition; ^1H NMR ($CDCl_3$) δ 1.98 (s, 12 H, Ar–CH_3), 2.12 (s, 12 H, Ar–CH_3), 6.80–7.80 (m, 15 H, Ar–H); ^{31}P NMR ($CDCl_3$) +158.7; ^{13}C NMR ($CDCl_3$) 200.2 (C1); IR (KBr) 1660 cm^{-1} (C=O); mass spectrum (70 eV), *m/e* (rel intensity, >20) 614 (M^+, 24), 378 (23), 377 (89), 361 (28), 254 (27), 240 (21), 239 (100), 237 (31), 222 (31), 221 (40), 220 (43), 134 (27), 121 (26), 44 (89), 28 (48).

Anal. Calcd for $C_{40}H_{39}O_4P$: C, 78.15; H, 6.40; P, 5.04. Found: C, 76.50; H, 6.10; P, 4.89.

3,4:8,9-Dibenzo-5,7-bis(trifluoromethyl)-1-phenyl-2,6,10,11-tetraoxa-1-phospha(V)tricyclo[5.3.1.0^{1,5}]undecane (2d). A solution of 0.92 mL (1.21 g, 0.0068 mol) of phenylphosphonous dichloride in 25 mL of THF was added dropwise to a stirred solution of 2.60 g (0.0137 mol) of 2-trifluoroacetylphenol[13] and 1.91 mL (1.39 g, 0.0137 mol) of triethylamine at −78 °C. The yellow reaction mixture was warmed slowly to 25 °C after the addition was completed. The yellow color faded on warming.

The solution was concentrated to 50 mL under reduced pressure and 25 mL hexane was added. The precipitated triethylamine hydrochloride (identified by ^1H NMR) was collected by filtration under N_2. The filtrate was stripped of solvent yielding a waxy off-white residue. Recrystallization from ethyl acetate/hexane yielded 1.40 g (46.0%) of phosphorane **2d** as fine colorless hygroscopic crystals: mp 154–156 °C; ^1H NMR ($CDCl_3$) δ 6.73–7.73 (m, 11 H, Ar–H), 8.17–8.50 (m, 2 H, H 3); ^{19}F NMR ($CDCl_3$) −76.0 (d of q, 3 F), −80.7 (q, 3 F, J_{FF} = 9 Hz) ppm; ^{31}P NMR ($CDCl_3$) −12.5 (q, J_{PF} = 7.0 Hz); mass spectrum (70 eV), *m/e* (rel intensity, >20) 487 ($M^+ + 1$, 30), 486 (M, 99), 446 (26), 389 (20), 297 (28), 212 (100), 183 (23), 165 (37), 152 (20), 127 (49), 77 (47), 28 (73).

Anal. Calcd for $C_{22}H_{13}F_6O_4P$: C, 54.33; H, 2.69; P, 6.37. Found: C, 53.98; H, 2.42; P, 6.50.

The filtrate was stripped of solvent and the gummy residue recrystallized from ethyl acetate/hexane to yield an additional 0.70 g (68.0% total) of phosphorane **2d**.

Bis(2-carbomethoxyphenyl) Phenylphosphonite (1f). A solution of 0.68 mL (0.90 g, 0.005 mol) of phenylphosphonous dichloride in 30 mL of THF was added dropwise to a stirred solution of 1.29 mL (1.52 g, 0.01 mol) of methyl salicylate and 1.40 mL (1.01 g, 0.01 mol) of triethylamine in 100 mL of THF at −78 °C. After the addition was completed, the reaction mixture was slowly warmed to 25 °C. The solution was concentrated to 25 mL under reduced pressure and 20 mL hexane was added. The precipitated triethylamine hydrochloride (identified by ^1H NMR) was collected by filtration under N_2.

The filtrate was stripped of solvent and the slightly viscous liquid residue was dissolved in ether/hexane and filtered through a dry Celite mat to remove a small amount of insoluble impurities. The filtrate was stripped of ether until the solution turned cloudy. The large colorless cubic crystals of phosphonous diester **1f** which formed on standing on −30 °C were collected by decanting the supernatant, washing twice with ether/hexane, and drying under high vacuum. The crystals, which liquefied on exposure to moist air, weighed 1.24 g (60.5%): mp 95.5–97.5 °C; ^1H NMR ($CDCl_3$) δ 3.73 (s, 6 H, Me), 6.93–7.53 (m, 9 H, Ar–H), 7.70–8.00 (m, 4 H, Ar–H); ^{13}C NMR ($CDCl_3$) 51.9 (s, $-OCH_3$), 121.8 (d, J_{PC} = 11 Hz, C6), 123.0 (d, J_{PC} = 2.4 Hz, C2), 123.5 (s, C4), 128.1 (d, J_{PC} = 7.0 Hz, C10), 130.4 (d, J_{PC} = 20.4 Hz, C9), 131.3 (s, C11), 131.7 (s, C3), 133.4 (s, C5), 139.3 (d, J_{PC} = 16.4 Hz, C8), 154.8 (d, J_{PC} = 3.9 Hz, C7), 166.2 (s, C1) ppm; ^{31}P NMR ($CDCl_3$) +161.7; electron impact mass spectrum (70 eV), *m/e* (rel intensity, >20) 396 (25), 395 (100, $M^+ - CH_3$), 275 (83), 259 (48); field desorption mass spectrum, *m/e* 410 (M^+).

Anal. Calcd for $C_{22}H_{19}O_6P$: C, 64.39; H, 4.67; P, 7.55. Found: C, 63.91; H, 4.81; P, 7.60.

The supernatant and washings were combined and stripped of solvent. The viscous liquid obtained was found by ^1H NMR to be largely unreacted methyl salicylate, although additional phosphonous diester **1f** was also present.

3,4:8,9-Dibenzo-6,11-dimethyl-1-phenyl-6,11-diaza-2,10-dioxa-1-phospha(V)tricyclo[5.3.1.0^{1,5}]undecane (8). A solution of 1.11 mL (1.43 g, 0.008 mol) of phenylphosphonous dichloride in 10 mL of THF was added dropwise to a stirred solution of 2.20 g (0.016 mol) of 2-(*N*-methylformimidoyl)phenol[14] and 2.28 mL (1.66 g, 0.016 mol) of triethylamine in 80 mL of THF at −78 °C. The cold bath was warmed slowly to 25 °C over an 8-h period. The solution was concentrated to 50 mL in vacuo and the precipitated triethylamine hydrochloride (identified by ^1H NMR) was collected by filtration under N_2.

The clear yellow filtrate was stripped of solvent to yield a gummy residue. Trituration with 30 mL of ether afforded 2.38 g (79.3%) of phosphorane **8** as a pale yellow powder (mp 136–141 °C). The filtrate was stripped of solvent and the residue was determined to be largely unreacted 2-(*N*-methylformimidoyl)phenol by ^1H NMR, although additional phosphorane was also present.

The crude product was recrystallized from ethyl acetate to yield pale yellow prisms: mp 169.5–171.5 °C; ^1H NMR ($CDCl_3$) δ 1.87 (d, 3 H, J_{PH} = 9.6 Hz, H4), 3.07 (d, 3 H, J_{PH} = 4.2 Hz, H3), 4.10 (d, 1 H, J_{PH} = 18.0 Hz, H1), 4.38 (d, 1 H, J_{PH} = 24.0 Hz, H2), 6.67–7.68 (m, 11 H, Ar–H), 7.88–8.20 (m, 2 H, H5); ^{13}C NMR ($CDCl_3$) 32.4 (d, J_{PC} = 3.8 Hz, C4), 48.7 (d, J_{PC} = 5.8 Hz, C3), 60.3 (d, J_{PC} = 115.3 Hz, C1), 83.6 (d, J_{PC} = 8.0 Hz, C2); ^{31}P NMR ($CDCl_3$) −1.7; mass spectrum (70 eV), *m/e* (rel intensity, >20) 376 (M^+, 35), 361 ($M^+ - CH_3$, 54), 243 (22), 242 (100), 165 (23), 135 (77), 134 (97), 120 (43), 118 (28), 91 (28), 77 (28), 60 (36), 42 (35), 32 (23), 28 (89).

Anal. Calcd for $C_{22}H_{21}N_2O_2P$: C, 70.20; H, 5.62; N, 7.44; P, 8.33. Found: C, 70.12; H, 5.71; N, 7.25; P, 8.24.

2-Bis(2′-carbomethoxyphenoxy)-2-phenyl-1,3,2-tetrachlorobenzodioxaphosphole (3). A 12-mm NMR tube was charged with 0.10 g (0.24 mmol) of phosphonous diester **1f** and 4 mL of $CDCl_3$. A single resonance at +161.7 ppm was observed in the ^{31}P NMR spectrum. Addition of 0.06 g (0.24 mmol) of tetrachloro-*o*-benzoquinone to the solution produced

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an intense ^{31}P NMR resonance at −41.8 ppm which replaced almost entirely the downfield resonance previously observed. The solution was stripped of solvent and the residue recrystallized from ethyl acetate to yield phosphorane **3** as large colorless prisms: mp 155–170 °C.

Anal. Calcd for $C_{28}H_{19}Cl_4O_8P$: C, 51.24; H, 2.92; Cl, 21.61; P, 4.72. Found: C, 50.36; H, 2.73; Cl, 21.95; P, 4.94.

2-Hydroxy-2′,4,4′-trimethoxybenzophenone. A mixture of 50.0 g (0.182 mol) of 2,2′-dihydroxy-4,4′-dimethoxybenzophenone, 25.8 g (0.182 mol) of methyl iodide, and 2.29 g (0.182 mol) of potassium carbonate in 250 mL of acetone was heated for 6 h at reflux. The reaction product obtained was determined to be a 1:1 mixture of starting material and 2-hydroxy-2′,4,4′-trimethoxybenzophenone by TLC and ^1H NMR. The mixture was heated at reflux for another 6 h in acetone with an additional 25.8 g (0.182 mol) of methyl iodide and 2.29 g (0.182 mol) of potassium carbonate. Addition of 100 mL of water caused yellow solids to precipitate. Recrystallization of the precipitated solids from methanol/acetone, following treatment with decolorizing carbon and hot filtration, yielded 36.0 g (68.6%) of 2-hydroxy-2′,4,4′-trimethoxybenzophenone as very pale yellow prisms: mp 110–111.5 °C (lit.[15] 104–105 °C); ^1H NMR ($CDCl_3$) δ 3.60 (s, 3 H, OMe), 3.70 (s, 3 H, OMe), 3.72 (s, 3 H, OMe), 6.10–6.47 (m, 4 H, Ar–H), 7.02–7.20 (m, 2 H, Ar–H), 12.67 (s, 1 H, Ar–OH, exchanges with D_2O); IR (KBr) 1610 cm^{-1} (C=O); mass spectrum (70 eV), *m/e* (rel intensity, >20) 288 (M^+, 22), 257 (100), 138 (84).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.60. Found: C, 66.87; H, 5.74.

An additional 6.7 g (81.4% total) of 2-hydroxy-2′,4,4′-trimethoxybenzophenone was isolated by concentration and recrystallization of the filtrate from methanol/acetone.

3,4:8,9-Bis(4′-methoxybenzo)-5,7-bis(2′,4′-dimethoxyphenyl)-1-phenyl-2,6,10,11-tetraoxa-1-phospha(V)tricyclo[5.3.1.0^{1,5}]undecane (5). A solution of 0.68 mL (1.31 g, 0.005 mol) of phenylphosphonous dichloride in 15 mL of THF was added dropwise to a stirred solution of 2.88 g (0.01 mol) of 2-hydroxy-2′,4,4′-trimethoxybenzophenone and 1.39 mL (1.01 g, 0.01 mol) of triethylamine in 60 mL of THF at −78 °C. The cold bath was removed 15 min after addition was completed and the cloudy yellow reaction mixture warmed slowly to 25 °C overnight. The precipitated triethylamine hydrochloride (1.37 g) was collected by filtration under N_2 and identified by ^1H NMR.

The clear yellow filtrate was evaporated and the residue was dissolved in ethyl acetate. Removal of solvent under reduced pressure caused colorless solids to precipitate. Following the addition of 10 mL of ether, 2.86 g (83.9%) of phosphorane **5** (mp 138–140 °C, with decomposition) was collected by filtration under N_2.

Purification was accomplished by recrystallization from ethyl acetate to yield small, colorless, slightly hygroscopic crystals: mp 143–145.5 °C, with decomposition; ^1H NMR (C_6D_6) δ 2.67 (s, 3 H, OMe), 3.07 (s, 3 H, OMe), 3.18 (s, 3 H, OMe), 3.28 (s, 6 H, OMe), 3.40 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 5.90–7.78 (m, Ar–H), 8.30–8.67 (m, 2 H, Ar–H ortho to P); ^{31}P NMR (C_6D_6) −18.6; mass spectrum (10 eV), *m/e* (rel intensity, >20) 682 (M^+, 3), 396 (34), 271 (25), 257 (100), 138 (86).

Anal. Calcd for $C_{38}H_{35}O_{10}P$: C, 66.86; H, 5.17; P, 4.54. Found: C, 67.04; H, 5.10; P, 4.49.

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Benzidine Rearrangements. 16. The Use of Heavy-Atom Kinetic Isotope Effects in Solving the Mechanism of the Acid-Catalyzed Rearrangement of Hydrazobenzene. The Concerted Pathway to Benzidine and the Nonconcerted Pathway to Diphenyline[1]

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Abstract: Kinetic isotope effects (KIE) in the acid-catalyzed rearrangement of hydrazobenzene (**1**) to benzidine (**2**) and diphenyline (**3**) have been measured. Nitrogen KIE were determined by whole-molecule mass spectrometry on each of the products obtained at low and 100% conversions from mixtures of **1** and [^{15}N,$^{15}N'$]**1**. The results were $k(^{14}N)/k(^{15}N)$ = 1.0222 for **2** and 1.0633 for **3**. Carbon KIE were determined with both ^{14}C and ^{13}C labeling, using counting techniques for the former and whole-molecule mass spectrometry for the latter. Again measurements were made on both products isolated from low and 100% conversions. Use of mixtures of **1** and [4-^{14}C]**1** gave $k(^{12}C)/k(^{14}C)$ = 1.0284 for **2** and 1.0011 for **3**. Use of mixtures of **1** and [4,4′-$^{13}C_2$]**1** gave $k(^{12}C)/k(^{13}C)$ = 1.0209 for **2** and 1.000 for **3**. The results show that the formation of **2** is a concerted process while the formation of **3** is a dissociative process involving the formation of an intermediate (possibly a π complex or pair of caged radical ions) in the rate-determining step. Calculations of the KIE were made on simplified models of transition states for concerted and dissociative processes and were found to be in reasonable agreement with the experimental results. In harmony with the concerted formation of **2** (the major product) we found also by whole-molecule mass spectrometry and with the use of mixtures of **1** and [4,4′-$^2H_2$]**1** that the disappearance of **1** has an inverse secondary deuterium KIE, $k(^1H)/k(^2H)$ = 0.962.

The acid-catalyzed rearrangements of hydrazoaromatics, described collectively as the benzidine rearrangement, have been known for over 100 years.[4] The rearrangements were long known to be intramolecular, and in the early years of mechanistic interest

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