Barriers to Pyramidal Inversion at Phosphorus in Phospholes, Phosphindoles, and Dibenzophospholes[1,2]

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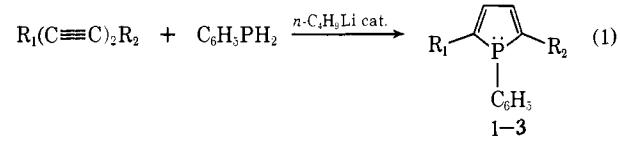
Abstract: Pyramidal inversion barriers ($\Delta G^{\ddagger}$) of variously substituted phospholes, a phosphindole, and a dibenzophosphole have been measured and compared with the inversion barriers of model compounds. It has been found that alkyl or aryl substituents do not significantly influence the unusually low barrier to pyramidal inversion (*ca.* 15–16 kcal/mol) at phosphorus in the phosphole system, but that mono- and diannulation (with a benzene ring) of the phosphole ring results in a significant increase in barrier height (*ca.* 8 and 10 kcal/mol, respectively), relative to the parent system. It is suggested that the low barrier to pyramidal inversion in phospholes is largely determined by stabilization which manifests itself to a greater extent in the planar transition state than in the pyramidal ground state, and which is ascribable to cyclic (3p–2p)π delocalization ("aromaticity"). The increase in barrier height which occurs upon annulation of the phosphole ring is attributed to a virtual disruption of the phosphole "aromaticity."

The planarity of pyrrole in the ground state[4] is attributable to maximal delocalization of the 6π electrons ("aromaticity") in the planar form, where the orbital axis of the lone electron pair on nitrogen is parallel to the orbital axes of the 2pπ electrons on carbon. In conformations of pyrrole containing a pyramidal nitrogen atom, p orbital overlap and π delocalization are reduced, the extent of reduction being related to the "degree of orthogonality" of the interacting orbitals.[5] These considerations, together with the greater pyramidal stability of phosphines, relative to the corresponding amines,[6] provided the impetus for the present study. The questions to which we addressed ourselves were: first, will the increase in aromatic stabilization associated with planar phosphole be sufficient to overcome the energy required to flatten the phosphorus pyramid, and thus lead to a planar ground-state conformation? Second, if the ground-state conformation of phosphole is not planar, *i.e.*, pyramidal, and the planar conformation thus becomes the transition state for inversion at phosphorus, to what extent will the increased aromaticity of the transition state make itself felt in a lowering of the inversion barrier? Surprisingly, with a single exception,[7] previous discussions[8,9] of phosphole aromaticity had not explicitly considered these questions concerning the geometry (planar *vs.* pyramidal) about phosphorus.

Nuclear magnetic resonance spectroscopy provides a convenient experimental technique for the investigation of these questions. First, the ground-state conformation of phospholes may be probed by incorporation of groups containing enantiotopic nuclei, which become diastereotopic in the chiral molecular environment that would be associated with appropriately substituted pyramidal phosphorus. Second, if phosphole is nonplanar, dynamic nuclear magnetic resonance (dnmr) spectroscopy may be used to measure the inversion barrier, if the activation energies are in the range of *ca.* 5–25 kcal/mol. To this end, variously substituted phospholes were prepared and analyzed by pmr. The syntheses of these compounds and model systems, the results of the investigation, and the discussion of the results are given in the following sections.

Syntheses

The phosphorus heterocycles used in the present study were prepared by direct extensions of reported methods. Phosphole ring systems with 1-phenyl substituents (**1–3**) were conveniently synthesized by the cyclization reaction reported by Märkl and Potthast,[9a] wherein substituted butadiynes and phenylphosphine combine according to eq 1. The synthesis of 1-benzyl-



(1)

1–**3**

1, $R_1 = CH_3$; $R_2 = C_6H_5$
2, $R_1 = CH_3$; $R_2 = (CH_2)_2C_6H_5$
3, $R_1 = CH(CH_3)_2$; $R_2 = C_6H_5$

2-methyl-5-phenylphosphole[10] from 1-phenyl-1,3-pentadiyne and benzylphosphine indicated that the exocyclic substituent bonded to phosphorus could be varied directly, by use of the appropriate phosphine. However, it was found that a more convenient method is the reaction represented by eq 2. Exocyclic carbon–phosphorus bond cleavage in **1** and **2** with lithium dispersion

(1) This work was supported by the Air Force Office of Scientific Research (AF-AFOSR-1188-B), by the National Science Foundation (GP-22542), and by Hoffmann–La Roche, Nutley, N. J.

(2) For a preliminary account of a portion of this work, see W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 1442 (1970).

(3) (a) National Aeronautics and Space Administration Fellow, 1969–1970; (b) National Defense Education Act Fellow, 1969; Public Health Service Predoctoral Fellow, 1969–1971.

(4) To fit the microwave spectrum of pyrrole, a planar conformation has been assumed: L. Nygaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, and G. O. Sørensen, *J. Mol. Struct.*, **3**, 491 (1969).

(5) M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, **91**, 2259 (1969).

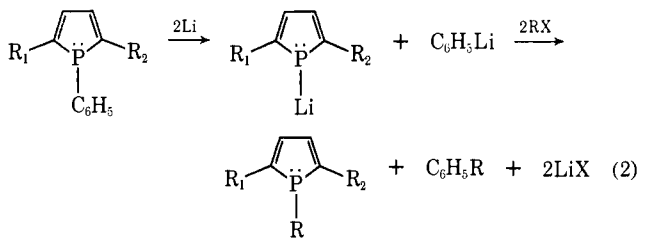
(6) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).

(7) D. A. Brown (*J. Chem. Soc.*, 929 (1962)) assumed that phosphole was planar in HMO calculations on this system.

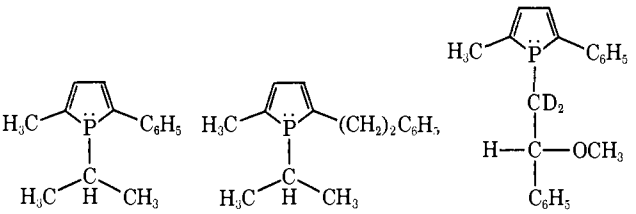
(8) (a) L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Amer. Chem. Soc.*, **91**, 3308 (1969); (b) A. F. Bedford, D. M. Heinekey, I. T. Millar, and C. T. Mortimer, *J. Chem. Soc.*, 2932 (1962); E. H. Braye and W. Hübel, *Chem. Ind. (London)*, 1250 (1959); F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *J. Amer. Chem. Soc.*, **82**, 5099 (1960); E. H. Braye, W. Hübel, and I. Caplier, *ibid.*, **83**, 4406 (1961); A. N. Hughes and S. Uaboonkul, *Tetrahedron*, **24**, 3437 (1968); K. W. Egger and T. L. James, *Trans. Faraday Soc.*, **66**, 2560 (1970).

(9) (a) G. Märkl and R. Potthast, *Angew. Chem.*, **79**, 58 (1967); (b) G. Märkl and R. Potthast, *Tetrahedron Lett.*, 1755 (1968).

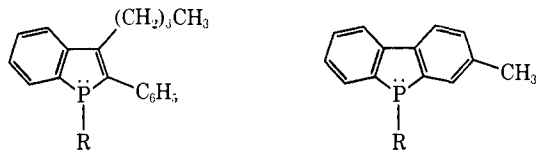
(10) R. Tang, Ph.D. Thesis, Princeton University, 1971.



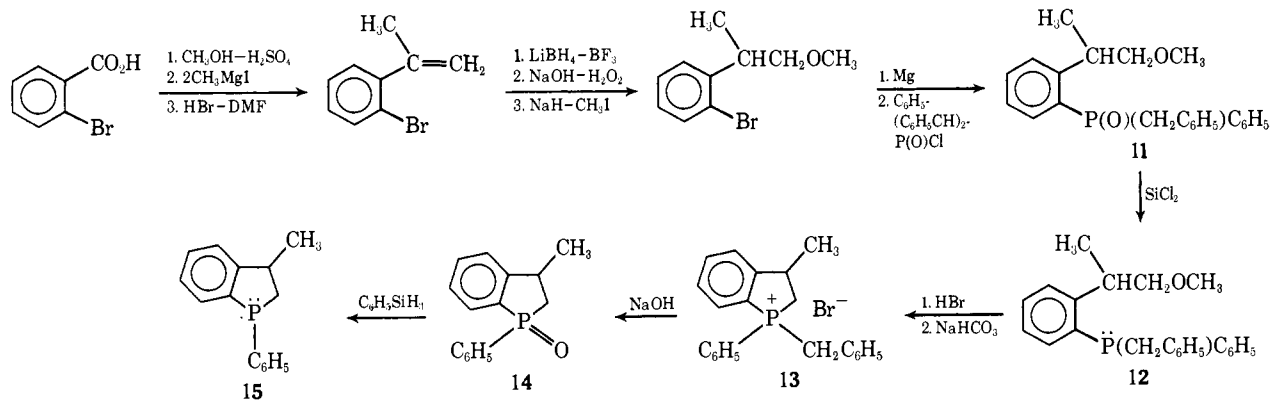
gave the respective 1-lithio derivatives, which were subsequently alkylated with an appropriate halide (RX).[11] For the purpose of the present study, the 1-lithio derivatives of **1** and **2** were treated with isopropyl bromide to give **4** and **5**, respectively, and the 1-lithio derivative of **1** was treated with racemic 2-phenyl-2-methoxyethyl-*1*-d_2 bromide[12] to give **6**.



4 **5** **6**

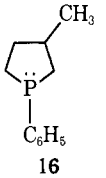


7, R = C_6H_5; **9**, R = C_6H_5
8, R = (*dl*)-$CD_2CH(OCH_3)C_6H_5$; **10**, R = (*dl*)-$CD_2CH(OCH_3)C_6H_5$



15 **14** **13** **12** **11**

A similar cleavage–alkylation sequence was used to convert 3-*n*-butyl-1,2-diphenylphosphindole (**7**) to **8** and 3-methyl-5-phenyldibenzophosphole (**9**) to **10**.



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The synthesis of 3-methyl-1-phenylphosphindoline (**15**) is summarized above. The key step in this preparation, the cyclization of **12** to **13**, was based by analogy on a report by Mann and Millar.[13]

The preparation of 3-methyl-1-phenylphospholane (**16**) has been described elsewhere[14] and details are given in the Experimental Section.

Results

The isopropyl methyl region of the pmr spectrum of **4** at 0.8° exhibits an eight-line absorption pattern corresponding to a conformationally restricted phosphole; the diastereotopic isopropyl methyls give rise to resonances centered at δ 1.02 ($^3J_{PH}$ = 13.9 Hz, $^3J_{HH}$ = 7.1 Hz) and 0.85 ($^3J_{PH}$ = 12.2 Hz, $^3J_{HH}$ = 7.1 Hz). The line shapes of these signals are temperature dependent, broadening with increasing temperature to a coalescence at *ca.* 42°; further heating results in a quartet.[15] The rate constants (k) at various temperatures were evaluated for this exchange process using Binsch's line-shape analysis program, DNMR.[16,17] Values of $\Delta H^{\ddagger}$ = 17.1 ± 0.4 kcal/mol and $\Delta S^{\ddagger}$ = 3.1 ± 1.1 eu were obtained from a least-squares treatment (nine data points, correlation coefficient 0.998) of ln (k/T) *vs.* ($1/T$) in the range 12–58°,[18,19] corresponding to $\Delta G^{\ddagger}_{42}$ = 16.1 kcal/mol (Table I). This exchange process corresponds to a first-order reaction as evidenced by the concentration-independent lifetimes.[20]

At −28° the isopropyl methyl region of the pmr spectrum of **5** also displays an eight-line pattern. The line shapes of these signals, like those of **4**, are temperature dependent, and increasing temperature produces a broadening of the signals until an eventual collapse to a broad quartet at 14°; further heating sharpens the quartet (see Figure 1).[17] Rate constants for the exchange process at 11 and 14° were determined by line-

(11) (a) E. H. Braye, U. S. Patent 3,338,941 (1967); *Chem. Abstr.*, **68**, 39816z (1968); (b) A. D. Britt and E. T. Kaiser, *J. Org. Chem.*, **31**, 112 (1966).

(12) (a) J. P. Casey, R. A. Lewis, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2789 (1969); (b) R. A. Lewis and K. Mislow, *ibid.*, **91**, 7009 (1969).

(13) F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 2205 (1951).

(14) W. Egan, G. Chauvière, K. Mislow, R. T. Clark, and K. L. Marsi, *Chem. Commun.*, 733 (1970).

(15) The pmr spectral tracings over this temperature range are presented in the preliminary communication; see ref 2.

(16) (a) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969); D. A. Kleier, G. Binsch, A. Steigel, and J. Sauer, *ibid.*, **92**, 3787 (1970). (b) The effective transverse relaxation time, T_2^{eff}, used throughout the temperature range in which the exchange rates were measured, was assumed to be constant and equal to the value determined at the slow-exchange limit: T. Drakenberg, K.-I. Dahlqvist, and S. Forsén (*Acta Chem. Scand.*, **24**, 694 (1970)) have noted that the spectral line shape near coalescence is insensitive to the exact value chosen for T_2^{eff}. The theoretical spectra were calculated assuming equal population of sites.

(17) Spectral changes were reversible and no decomposition products were detected by pmr.

(18) The transmission coefficient was assumed to be unity; see G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

(19) The error values reported for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are standard deviations. The actual errors are most likely greater than statistical; see A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).

(20) The pmr spectral tracings over the concentration range tested (7–25% v/v solution in $CFCl_3$) are recorded in ref 10.

Table I. Rate and Equilibrium Parameters for Phospholes and Related Systems

Compd	Solvent	$\Delta G^{\ddagger}$,[a] kcal/mol	T,[b] °C	K[c]	$\Delta\nu_{AB}$,[d] Hz
3	$CFCl_3$	≥ 15[e]			
4	$CFCl_3$	16.1[f,g]	42.3		15.8[h]
5	$CFCl_3$	16.1[g,i]	11.0		2.7[h]
		16.0	14.0		2.1
6	$CFCl_3$	15.3[i,k]	1.3[l]	1.22	2.0[m]
		15.2			
8	$1,2\text{-}(CD_3)_2C_6H_4$	23.7[i,k]	165.0[l]	1.20	8.5[m]
		23.5			
	C_6H_5CN	23.3[i,k]	153.8[l]	1.22	6.3[m]
		23.1			
10	C_6H_6	26.3[k,n]	59.8[o]	1.05	
		26.2			
15	C_6D_6	35.3[k,n]	130.0[o]	1.64	
		34.9			
16	C_6H_6	36.5[k,n]	170.0[o]	1.27	
		36.3			

[a] Calculated from the Eyring equation, at T. The estimated error is ±0.5 kcal/mol. [b] Accurate to ±2° for **3**–**8**; ±0.05° for **10**; ±0.5° for **15** and **16**. [c] Accurate to ±0.05. [d] Accurate to ±0.1 Hz. [e] Calculated from a rate constant derived from the Gutowsky–Holm equation, assuming coalescence at 1.8° with $\Delta\nu_{AB}$ (100 MHz) = 1.1 Hz; see text. [f] Calculated from $\Delta H^{\ddagger}$ = 17.1 kcal/mol and $\Delta S^{\ddagger}$ = 3.1 eu. [g] Calculated from a complete line-shape analysis, see ref 16. [h] At 100 MHz. [i] The two values of $\Delta G^{\ddagger}$ were derived from the two coalescence phenomena observed for **5**; see text. [j] Calculated from the coalescence formulas in ref 23. [k] Values for both diastereomers are given. [l] Coalescence temperature. [m] At 60 MHz. [n] Calculated from rate constants determined by the equilibration method; see ref 25 and 28. [o] Temperature at which equilibration was carried out.

shape analysis,[16] and substitution of these rate constants into the Eyring equation yielded the values of $\Delta G^{\ddagger}$ presented for **5** in Table I.

In contrast to **4** which exhibits a single broad coalescence peak at *ca.* 42°, **5** exhibits (Figure 1) coalescences of the two upfield doublets to a single doublet at 11° and of the two downfield doublets to a single doublet at 14°. These two separate coalescences are the result of a combination of factors: the nonequivalence of the two $^3J_{PH}$ values, the accidental equivalence of the two $^3J_{HH}$ values, and a chemical-shift difference between signals due to the isopropyl methyl protons ($\Delta\nu_{AB}$) that is less than either $^3J_{PH}$ or $^3J_{HH}$. On the other hand, the single broad coalescence signal found for **4** results from the circumstance that $\Delta\nu_{AB}$ is greater than either $^3J_{PH}$ or $^3J_{HH}$.

Use of the Gutowsky–Holm equation, $k_c = (\pi/\sqrt{2})\cdot\Delta\nu_{AB}$,[21] to obtain rate constants for the site exchange of the isopropyl methyl group protons in both **4** and **5** leads to values for $\Delta G^{\ddagger}$ which essentially equal (within ±0.4 kcal/mol) those calculated using exchange rate constants obtained from complete line-shape analysis. For **4** and **5**, the values used as $\Delta\nu_{AB}$ are large (17.0 Hz) and small (2.1 and 2.7 Hz), respectively, relative to the slow-exchange line widths at half-height (*ca.* 0.8 Hz), and it is thus expected[21] that rate constants obtained from the Gutowsky–Holm equation should be more accurately determined for **4** than for **5**. On the other hand, temperatures at coalescence are more accurately assigned to **5** than to **4**. Since both rate constant and temperature are input for the Eyring equation, it is difficult to assess which case should yield the more accurate approximate $\Delta G^{\ddagger}$ value. The relatively close agreement between $\Delta G^{\ddagger}$ values derived from rate constants calculated by approximate and exact methods is a consequence of the insensitivity of $\Delta G^{\ddagger}$ to the difference in rate constants obtainable by the two procedures. Thus, within the usual pmr rate (*ca.* 1–100 sec^{-1}) and temperature (−100 to 200°) range, a factor of two in rate constant corresponds to a difference of only *ca.* 0.5 kcal/mol in $\Delta G^{\ddagger}$. It thus appears that, even in complex spin systems, a relatively accurate estimate of $\Delta G^{\ddagger}$ may be obtained without recourse to a complete line-shape analysis.[22a]

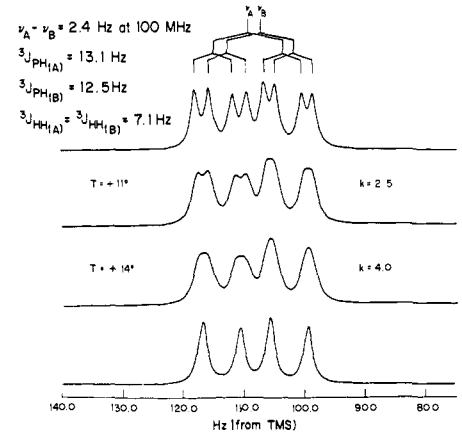


Figure 1. Simulated pmr spectra for the isopropyl methyl protons in **5** at various exchange rates (k), representing the best fits to the experimental pmr spectra for **5** at the temperatures indicated. The chemical shifts of the diastereotopic isopropyl methyl groups are ν_A and ν_B.

The pmr spectrum of the isopropyl methyl region of **3** at −9.1° consists of two doublets ($\Delta\nu_{AB}$ = 1.1 Hz; $^3J_{HH}$ = 6.6 Hz), which collapse to a doublet ($^3J_{HH}$ = 6.6 Hz) at 1.8°.[17] However, because of the small signal separation, we were unable to distinguish exchange-induced coalescence from signal coincidence due to a change in chemical shift with temperature. Consequently, the value of $\Delta G^{\ddagger}$ reported in Table I, which was calculated on the assumption of an exchange-induced coalescence, may represent only a lower limit.

The pmr spectrum of **6** at −9° (Figure 2) also gave the expected pattern for a conformationally restricted phosphole. Resonance doubling is due to the sensor nuclei that are diastereotopic by external comparison, as evidenced by the unequal signal intensities for corresponding absorptions. Coalescence of the anisochronous methoxy signals of **6** at 1.3° corresponds to the exchange of two uncoupled, unequally populated sites, and exact (assuming $1/T_2$ = 0) first-order rate constants for this conformational exchange process are readily calculated.[23]

(21) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956). The values of $\Delta\nu_{AB}$ chosen for **5** were the separations (2.1 and 2.7 Hz) at the slow-exchange limit of the appropriate spin-multiplet components whose coalescences were observed.[22] For **4**, $\Delta\nu_{AB}$ is equal to the chemical-shift difference at the slow-exchange limit.

(22) For similar examples, see B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38**, 681 (1960); T. H. Siddall, III, W. E. Stewart, and F. D. Knight, *J. Phys. Chem.*, **74**, 3580 (1970); F. J. Weigert, M. B. Winstead, J. I. Garrels, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7359 (1970).

(22a) NOTE ADDED IN PROOF. See also D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

(23) H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 961 (1970). Solution (Newton–Raphson method) of eq 1 of this reference, a sixth-order polynomial, for each value of ΔP from 0.00 to 1.00 in 0.01 increments, resulted in no more than two real and positive roots for each value of ΔP. Choice of the proper root was obvious by inspec-

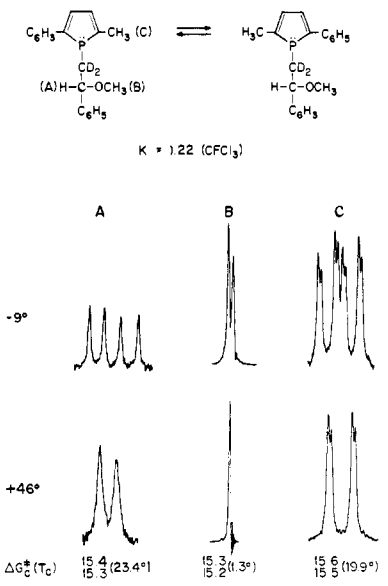


Figure 2. Pmr spectral tracings for **6** ($CFCl_3$ solvent; 60 MHz). Upper composite: slow site exchange (−9°); chemical-shift differences between the diastereotopic protons of the A, B, and C sensor nuclei are 15.0, 2.0, and 7.6 Hz, respectively. Lower composite: rapid site exchange (+46°). Values of $\Delta G^{\ddagger}_{c}$ for diastereomerization of **6** refer to T_c.

As shown in Figure 2, coalescence phenomena[17] were also observed for the signals due to the methine, as well as the ring methyl protons of the diastereomers of **6**. The $\Delta G^{\ddagger}$ values reported in Table I were determined[23] from the coalescence of the methoxy signals; the two remaining sets of values for $\Delta G^{\ddagger}$ given in Figure 2 were obtained from rate constants approximated by the unequal doublet equation.[23] Agreement among the three sets of $\Delta G^{\ddagger}$ values determined for **6** is within experimental error.

Phosphindole **8**, in 1,2-$(CD_3)_2C_6H_4$ solvent, exhibits a temperature-dependent pmr spectrum analogous to that of **6**; coalescence[17] of the unequally populated, anisochronous signals due to the diastereotopic methoxy groups occurred at 165°. Values of $\Delta G^{\ddagger}_{165}$ for **8** (Table I) were calculated in the same manner as for **6**.[23] Determination of $\Delta G^{\ddagger}$ for **8** in a more polar solvent, benzonitrile, yielded values of $\Delta G^{\ddagger}$ (Table I) which were insignificantly different from those obtained in the deuterated *o*-xylene.

For **6** and **8**, in the temperature ranges of −36 to −16° and 48 to 113°, respectively, mutual site exchange is slow on the pmr time scale. For each compound, the equilibrium constant (K), which is equal to the ratio of the pmr signals due to the methoxy protons, was evaluated by electronic integration and/or peak height measurement. The equilibrium constants for **6** and **8** were found to be, within experimental error, temperature independent; the value of K at the coalescence temperature was assumed to be equal to the value determined at lower temperatures.[24]

With the exception of **5**, compounds studied by dnmr exhibited temperature-dependent chemical shifts. The complexity of the isopropyl methyl region of the pmr spectra of **4** allows ready discernment of a slight decrease (1.2 Hz) in chemical shift with increasing temperature over the range in which rate constants were determined. Thus, uncertainty in the chemical-shift difference between the coalescing signals was not a factor lessening the accuracy of the calculated rate constants, as it may be in, for example, a simple uncoupled AB spin system.[26] For **6** and **8**, the chemical-shift difference between the methoxy signals at the coalescence temperature was determined by extrapolation from a plot of $\Delta\nu_{AB}$ *vs.* temperature, and by assuming[27] that the spectral line width at half-height at coalescence is equal to $\Delta\nu_{AB}$. For both **6** and **8**, values of $\Delta\nu_{AB}$ determined by these two procedures afforded values of $\Delta G^{\ddagger}$ which differed by less than 0.1 kcal/mol. The average values of $\Delta\nu_{AB}$ and $\Delta G^{\ddagger}$ for **6** and for **8** are reported in Table I.

Conformational restriction in **10** at 40° gave rise to a pmr spectrum at 60 MHz which, in a variety of solvents, exhibited anisochrony of only the methine proton signals ($\Delta\nu_{AB}$ = *ca.* 3 Hz). A lower limit of $\Delta G^{\ddagger}$ = *ca.* 22 kcal/mol for the conformational exchange process in **10** follows from the observation that anisochrony of the methine signals is still observable at 130°.

Equilibration methods were therefore used to obtain values for the rate constants associated with the conformational exchange process in **10**. The starting material was a nonequilibrium mixture of the diastereomers of **10**, prepared by stereospecific phenylsilane reduction of a diastereomerically enriched mixture of the corresponding 1-oxides (**17**). The sum of the forward (k_1) and reverse (k_{-1}) rate constants for the equilibration of the diastereomers of **10** at 59.8° was calculated by use of eq 3, which is an adaptation[25] of the usual expression[28] for a reversible first-order reaction

$$\ln [(R - K)/(1 + R)] = -(k_1 + k_{-1})t \qquad (3)$$

where R is the ratio of diastereomers at time t and K is the equilibrium constant (*i.e.*, R at t_∞). From K and the calculated value of $(k_1 + k_{-1})$, values for k_1 and k_{-1} and hence $\Delta G^{\ddagger}_1$ and $\Delta G^{\ddagger}_{-1}$ for the diastereomers of **10** were readily determined (Table I). The small chemical-shift difference between the methine protons of the diastereomers of **10**, together with coupling of these protons to both phosphorus ($^3J_{PH}$ = *ca.* 7.5 Hz) and deuterium ($^3J_{HD}$ = *ca.* 1 Hz) precluded convenient use of the methine proton signals for accurate measurement of R. Consequently, values of R were determined by stereospecific oxidation of **10** to **17** (see Experimental Section) with hydrogen peroxide, followed by measurement of the relative intensities of the pmr signals due to the ring methyl protons in **17**.

Values of $\Delta G^{\ddagger}$ for pyramidal inversion in **15** and **16** (Table I) were also calculated from rate constants obtained by equilibration methods, using diastereomerically enriched mixtures of **15** and of **16**, which had been prepared by phenylsilane reduction of enriched mixtures of

tion. This procedure eliminates the need for the graphical solution that is described in the above reference. A table of these roots is available on request.

(24) A similar finding and assumption have been reported by Gutowsky, *et al.*,[25] for *cis*- and *trans*-*N*-benzyl-*N*-methylformamide.

(25) H. S. Gutowsky, J. Jonas, and T. H. Siddall, III, *J. Amer. Chem. Soc.*, **89**, 4300 (1967).

(26) The desirability of a complex spectrum, when performing a complete line-shape analysis, has been previously noted;[16a] *cf.* also, K.-I. Dahlqvist and S. Forsén, *Acta Chem. Scand.*, **24**, 651 (1970); K.-I. Dahlqvist and S. Forsén, *J. Magn. Resonance*, **2**, 61 (1970).

(27) Although this assumption is valid only when the populations of the A and B sites are equal,[20] it is most likely a good approximation for **6** and **8** since ΔP[23] was only 0.1.

(28) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill, New York, N. Y., 1965, p 20.

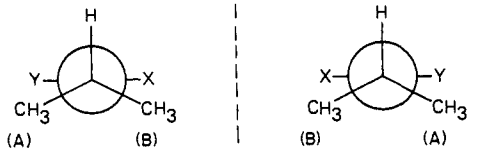
their corresponding oxides, **14** and **18**, respectively. For **15**, the kinetic study was performed at 130° and values of R were obtained by rapid cooling of the sample to room temperature and measurement (at *ca.* 40°) of the relative pmr absorption intensities of the methyl protons. A similar procedure was not possible for **16**, due to the overlap of the pmr signals of the ring methylene protons with those of the methyl protons. Removal and rapid cooling of aliquots of **16**, which were maintained at 170°, followed by stereospecific quaternization with methylene iodide, gave diastereomeric 1-iodomethyl-3-methyl-1-phenylphospholanium iodides (**19**). This mixture of derivatives could be quantitatively analyzed by pmr for values of R, using the relative signal intensities of the iodomethyl protons, which were shifted downfield relative to the ring methylene proton signals.

Further details of kinetic studies are supplied in the Experimental Section.

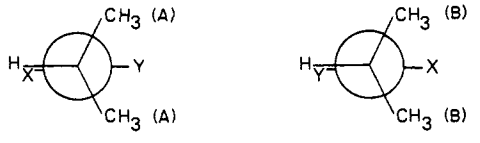
Discussion

The pmr spectra of the isopropyl methyl protons in phospholes **3**–**5**, in the slow-exchange limit, are accommodated by alternative interpretations: in case I, the phosphorus atom and the three atoms bonded to it form a planar array (or pyramidal inversion is rapid on the nmr time scale), whereas in case II, the phosphorus atom is pyramidal, and pyramidal inversion is slow on the nmr time scale.

For case I, two hypothetical possibilities may be envisaged: either a racemic mixture of a single chiral isomer (case Ia) predominates, in which the isopropyl methyl groups are diastereotopic by internal comparison, or two accidentally equally populated achiral diastereomers (case Ib) exist in which the isopropyl groups are diastereotopic by external comparison; in both cases, rotation about the bond linking the isopropyl group to the ring is slow on the nmr time scale.



Ia



Ib

In case II, on the other hand, the phosphorus atom is a chiral center and the isopropyl methyl groups are diastereotopic in all torsional conformations. Thus, any number of isomers that are rapidly interconverting by rotation can give rise to the observed low-temperature spectra.[29]

(29) Additional interpretations may be advanced for cases I and II, but these require an unreasonable number of accidental degeneracies. They are therefore regarded as highly improbable and are not discussed in this paper.

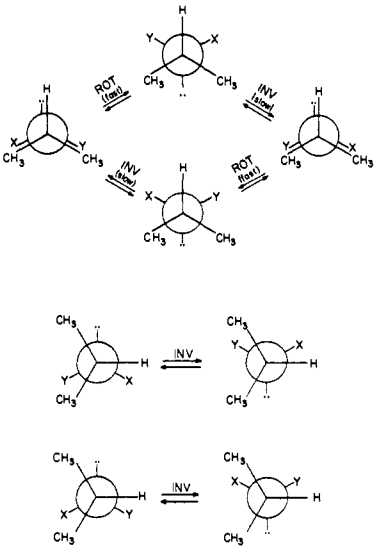


Figure 3. Schematics for the conformational interconversion of chiral *P*-isopropylphospholes by pyramidal inversion (case II, see text): top, with additional torsional modes; bottom, without torsion.

The following observations militate against case Ib. The phosphole ring protons in the isomers of **3**–**5** and the ring methyl protons in the isomers of **4** and **5** are diastereotopic by external comparison, yet no resonance doubling of the pmr signals was observed. By contrast, where diastereomers must exist (see **6**, preceding section), resonance doubling of the phosphole ring protons (see Experimental Section) and of the ring methyl protons (Figure 2) is observed. These spectral findings may be taken as evidence against case Ib, for it is highly improbable that such fortuitous spectral coincidence should exist *in all three* compounds. Furthermore, in **6** the ratio of diastereomers differs observably from unity, and the hypothesis that the ratio is unity in case Ib may therefore be regarded as weak.

While considerations based on symmetry criteria cannot distinguish between cases Ia and II, the approximate constancy of the measured barrier height ($\Delta G^{\ddagger}$ *ca.* 16 kcal/mol) for **3**–**6** renders interpretations involving a rate-determining torsional process (*i.e.*, Ia) highly unlikely, given the widely differing structures of these four compounds. Furthermore, reported data[30] suggest that a barrier height of *ca.* 16 kcal/mol is far too high for restricted torsion about the phosphorus–carbon bond in **4**–**6**.[31] We therefore conclude that the ground-state conformation of phospholes is nonplanar,[32] and that pyramidal inversion at phosphorus is the rate-determining conformational exchange process (see Figure 3) which corresponds to the measured barrier[33] (case II). By extension, a similar conclusion ob-

(30) Even in a severely hindered system such as tris(2,4,6-trimethylphenyl)phosphine, the rotational barrier about the phosphorus–carbon bond is only *ca.* 12 kcal/mol (A. Reiker and H. Kessler, *Tetrahedron Lett.*, 1227 (1969); *cf.* also, W. McFarlane, *Chem. Commun.*, 229 (1968)).

(31) Cooling a sample of **4** to *ca.* −100° (CF_2Cl_2 solvent) produces only a broadening of the resonances and no new signals, while tetramethylsilane remains relatively sharp.

(32) Subsequent to our preliminary communication,[2] this conclusion was confirmed by an X-ray analysis (P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, **92**, 5779 (1970)) which showed that the geometry about phosphorus in 1-benzylphosphole is pyramidal.

(33) This assignment is also in accord with results obtained in a

tains for phosphindoles,[33] *e.g.*, **8**, and dibenzophospholes, *e.g.*, **10**.

The inversion barriers measured for **3–6** are the lowest reported for a phosphine. Comparison of these barrier heights with that estimated for a hypothetical system in which *cyclic* π delocalization is absent should throw some light on our initial question regarding the aromaticity of phospholes. A crude estimate for such a localized analog may be obtained as follows. Replacement of an alkyl group by an aryl group in acyclic dialkylarylphosphines results in a *ca.* 2 kcal/mol lowering of the inversion barrier due to (3p–2p) π delocalization.[34] Assuming that a similar lowering obtains following substitution of an alkyl group by an ethylenic group, the estimated inversion barrier for the hypothetical phosphole thus becomes *ca.* 34 kcal/mol, based on the barrier found for **16** (36 kcal/mol). The experimentally measured inversion barriers for phospholes **3–6** are thus approximately 18 kcal/mol lower than the estimated value.[35] This lowering may be rationalized in only three ways: preferential raising of the ground state relative to the transition state (case A), raising the ground state in concert with a lowering of the transition state (case B), or a preferential lowering of the transition state relative to the ground state (case C). In the present context, from the viewpoint of π-conjugative effects, cases A and B refer to an "antiaromatic"[37] ground state, while case C may be considered to reflect behavior expected of an aromatic Hückel 6π-electron system. In the absence of precedent, experimental or theoretical, for believing that phospholes should possess an antiaromatic ground state, we have chosen to discuss our results in terms of case C.[38] Moreover, by analogy to pyrrole and thiophene, both of which are believed to possess aromatic ground states,[42] it is only reasonable to expect that phosphole possesses an aromatic ground state also. We conclude that the lowered inversion barriers found for **3–6** indicate that phospholes are Hückel 6π-electron systems in which electron delocalization is at a maximum[43] in the planar transition state,[44,46] relative to the pyramidal ground state.[47]

Using the previous assumption regarding the equality of π-conjugative effects for ethylenic and phenyl groups, the estimated inversion barrier for a hypothetical phosphindole is approximately equal to that measured for **15** (*ca.* 35 kcal/mol). Thus, the experimentally measured inversion barrier for phosphindole **8** is roughly 11 kcal/mol lower than the estimated value.[46]

Inversion barriers for diarylalkylphosphines are *ca.* 30 kcal/mol.[34] Increased angle strain in the transition state to inversion, resulting from incorporation of a phosphorus atom into a five-membered ring, causes an increase in barrier height of *ca.* 4 kcal/mol.[49] Assuming an approximate additivity of effects, a barrier of *ca.* 34 kcal/mol is expected for **10**, which may be thought of as having been formed by joining the two ortho positions of the phenyl rings of a diarylalkylphosphine to construct the five-membered dibenzophosphole ring system. The difference between the estimated and measured barrier for **10** is therefore approximately 8 kcal/mol.[44,46]

The significant increase in barrier heights measured for the phosphindole and dibenzophosphole ring systems, relative to the parent phosphole ring system, may be attributed, at a heuristic level of description, to an increased disruption of the phosphole aromaticity in the planar transition state[44,46] relative to the pyramidal ground state, in these annulated systems. This increasing diminution of net aromatic stabilization associated with the phosphole moiety parallels the analogous trend among the calculated values for the resonance energies of pyrrole, indole, and carbazole,[42a] as well as for the resonance energies of thiophene, 2,3-

semiempirical theoretical calculation (A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, in press; J. D. Andose, Ph.D. Thesis, Princeton University, 1971).

(34) R. D. Baechler and K. Mislow, *ibid.*, **92**, 3090 (1970).

(35) The value of $\Delta S^{\ddagger}$ measured for **4** is not significantly different from 0 eu, as expected[34] for pyramidal inversion at phosphorus. Values of $\Delta G^{\ddagger}$ determined at different temperatures may thus be directly compared. Errors introduced by this assumption, as well as by solvent effects,[36] are believed to be small.

(36) H. D. Munro and L. Horner, *Tetrahedron*, **26**, 4621 (1970).

(37) The terms aromatic and antiaromatic are defined in the thermodynamic sense; for a discussion of this subject, and leading references, see R. Breslow, *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968), and R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

(38) It has been recently suggested[39] that the low inversion barrier found for a substituted thiophene 1-oxide may be the result of "relief from a destabilization energy associated with the (antiaromatic) pyramidal form." The reason offered for suggesting this possibility arose, in part, from the observation that thiophene 1-oxides (unless severely sterically hindered) readily undergo thermal (4 + 2) cycloadditions, a characteristic of certain antiaromatic systems. Sulfur d orbitals were invoked[39] to construct the antiaromatic ground state, as is reasonable when the ligands attached to sulfur are highly electronegative.[40] However, in contrast to thiophene 1-oxides, phospholes are stable to thermal dimerization[41] and, as the phospholes of this study do not possess highly electronegative ligands bonded to phosphorus, 3d-orbital contraction to facilitate overlap with adjacent carbon 2p orbitals is not anticipated.

(39) W. L. Mock, *J. Amer. Chem. Soc.*, **92**, 7610 (1970).

(40) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

(41) For example, 1-methylphosphole is a stable well-characterized substance.[8a]

(42) (a) M. J. S. Dewar, A. J. Harget, N. Trinajstić, and S. D. Worley, *Tetrahedron*, **26**, 4505 (1970); (b) M. J. S. Dewar and N. Trinajstić, *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

(43) By use of a simple geometric argument, it has been shown[5] that the lone electron pair on pyramidal nitrogen can conjugate effectively with an adjacent carbon 2p orbital, the resonance energy being about four-fifths that for the planar system. This argument is likewise valid for the phosphorus analog.

(44) Enantiomerization or automerization (*i.e.*, the interconversion of molecules related by an isometry) must perforce give rise to a transition state with local planarity,[45] given a double-well potential surface for the pyramidal inversion process. For the interconversion of all remaining sets of molecules, *i.e.*, of diastereomers, the probability of a locally planar transition state is vanishingly small. However, since $\Delta\Delta G^{\ddagger}$ measured for the interconversion of diastereomeric pairs of phospholes does not exceed 0.2 kcal/mol (**6**, **8**, and **10**; see Table I), the energy profile, though recognized to be skewed, probably does not deviate significantly from that of a symmetric pathway, and the transition state to inversion is probably nearly planar.[46]

(45) *Locally planar* refers to the inverting center and its immediately bonded atoms.

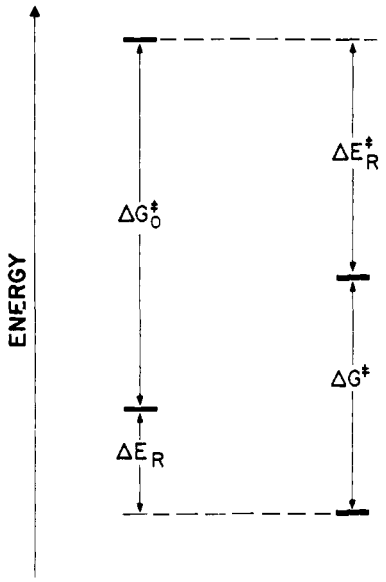
(46) For the phosphole inversion process, the absence of an intermediate is assumed. Although the nmr experiment does not permit a decision on this point, we note that to the extent that an intermediate *does* intervene, the observed degree of aromaticity represents a lower limit.

(47) Cyclic π delocalization in the phosphole ground state must be accompanied by an increased bond order between carbon atoms 3 and 4, relative to a hypothetical undelocalized system, and this should be reflected in the ^3J values between the hydrogen atoms on C-3 and C-4; an increase in absolute values of J should accompany an increase in bond order. In phospholes **4** and **3** the opposite trend was observed: a value of 3.0 (±0.1) Hz was found for both **4** and **3**, whereas values of 3.6 (±0.2) Hz and 3.8 (±0.1) Hz were found for the corresponding sulfides, which might be regarded as undelocalized models. However, this behavior may be ascribed principally to differences in inductive effects, as well as to the failure of the phosphole sulfides to mimic the ring geometry of an undelocalized phosphole.[48]

(48) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **91**, 6325 (1969).

(49) This value derives from a comparison of the barrier height for **16** (36 kcal/mol) with that for an acyclic dialkylarylphosphine (32 kcal/mol[34]).

benzothiophene, and dibenzothiophene.[42b] Although our conclusion regarding the effect of annulation on phosphole aromaticity derives from a consideration of inversion barriers, whereas calculated[42] resonance energies refer only to ground states, the parallel trends may be rationalized by reference to the following diagram ($\Delta G^{\ddagger}_0$ = estimated inversion barrier for a



hypothetical model system in which cyclic π delocalization in the phosphole moiety is absent; $\Delta G^{\ddagger}$ = measured inversion barrier for a phosphole, phosphindole, or dibenzophosphole; $\Delta E_R{}^{\ddagger}$ = resonance stabilization of the planar phosphole moiety; ΔE_R = resonance stabilization of the pyramidal phosphole moiety).

For case C, using the above definitions,

$$\Delta G^{\ddagger}_0 - \Delta G^{\ddagger} = \Delta E_R{}^{\ddagger} - \Delta E_R \qquad (4)$$

Let

$$f = \Delta E_R/\Delta E_R{}^{\ddagger}$$

then

$$\Delta G^{\ddagger}_0 - \Delta G^{\ddagger} = \Delta E_R{}^{\ddagger}(1 - f) \qquad (5)$$

From eq 5, it follows that the trend observed among differences in estimated and measured barrier heights ($\Delta G^{\ddagger}_0 - \Delta G^{\ddagger}$) for the phosphole, phosphindole, and dibenzophosphole ring systems parallels the trend of the relative resonance stabilization of the five-membered heterocyclic moiety of the analogous nitrogen[42a] and sulfur[42b] series, to the extent that f remains constant. Since the values of f are dependent only on geometry, *i.e.*, out-of-plane angle, it is not unreasonable to expect approximate constancy in the phosphole, phosphindole, and dibenzophosphole series.

Experimental Section[50]

1-Phenyl-1,3-pentadiyne was synthesized by a modification of the procedure reported by Taniguchi, *et al.*[51] Phenylacetylene (88 ml, 0.8 mol) was added to a solution of ethylmagnesium bromide, prepared from ethyl bromide (60 ml, 0.8 mol) and magnesium turnings (16 g, 0.66 mol) in tetrahydrofuran (THF; 200 ml) at a rate sufficient to maintain reflux. After addition was completed, the reaction mixture was heated at *ca.* 70° for 1 hr. A catalytic amount of cuprous chloride (2 g, 20 mmol) was added to the reaction mixture, which was cooled to room temperature, and reflux was continued for 1 hr. A solution of propargyl bromide (42 ml, 0.53 mol) in THF (100 ml) was added to the refluxing reaction mixture over a period of *ca.* 0.5 hr and after addition was completed, the mixture was refluxed for *ca.* 20 min. The cooled (40–50°) reaction mixture was poured onto ice (500 g) and water (500 ml) and acidified with concentrated sulfuric acid (50 ml). The aqueous layer was extracted twice with 250-ml portions of ether and the combined organic layers were neutralized with an aqueous solution of sodium bicarbonate and washed with a saturated solution of aqueous sodium chloride. Solvent was removed from the dried (sodium sulfate) organic layer, using a rotary evaporator, to yield crude 1-phenyl-1,4-pentadiyne as a dark orange oil. This material was added to a cold (*ca.* 0°) solution of potassium hydroxide (0.53 mol) in anhydrous ethanol (*ca.* 400 ml) and stirred at this temperature for 3 hr. The reaction mixture was treated with concentrated hydrochloric acid (*ca.* 50 ml) and was diluted with benzene (300 ml). The separated organic layer was washed twice with saturated aqueous sodium chloride and dried (sodium sulfate). Removal of solvent on a rotary evaporator gave a dark brown oil, which was kugelrohr distilled to yield a light brown oil, bp *ca.* 120° (0.1 mm). (*Caution:* Very rapid pyrolysis occurred above *ca.* 120°.) Redistillation (kugelrohr) gave the desired product as a pale yellow oil (44 g, 60%), bp *ca.* 105° (0.1 mm) (lit.[51] bp 120° (0.2 mm)), which was judged to be >95% pure by pmr analysis.[51]

2-Methyl-6-phenyl-3,5-hexadiyne. The following preparation was adapted from Hay.[52] Isopropylacetylene (100 g, 1.47 mol) and phenylacetylene (30 g, 0.294 mol) were mixed at 0° with cuprous chloride (8 g, 80 mmol), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; 8 g, 70 mmol), pyridine (100 ml), anhydrous ether (450 ml), and acetone (250 ml) in a flask equipped with a Dry Ice condenser and a mechanical stirrer. The reaction was maintained at *ca.* 0° for 2 days and then at room temperature for 4 days. During this period, a slow stream of oxygen was continuously passed through the reaction mixture. The reaction mixture was quenched with water, diluted with ether, and extracted with water until the aqueous washings were no longer green. Solvent was removed from the dried (sodium sulfate) organic layer at reduced pressure and volatiles were removed under high vacuum. The residual oil was diluted with 30–60° petroleum ether and cooled to *ca.* 5°; crystals of diphenyldiacetylene were obtained upon seeding, and were separated. After most of the diphenyldiacetylene was removed by repeated crystallization, distillation of the mother liquor gave 2-methyl-6-phenyl-3,5-hexadiyne (20 g, 40%): bp 131° (2 mm); pmr δ 1.22 (d, $^3J_{HH}$ = 6.5 Hz, $CH(CH_3)_2$), 2.33–3.16 (septet, $^3J_{HH}$ = 6.5 Hz, $CH(CH_3)_2$), and 7.0–7.6 (m, C_6H_5). The mass spectrum of this product was consistent with its assigned structure and the ir spectrum featured absorptions at 2240 (s) and 2150 cm^{-1} (w), presumably due to the acetylenic stretch.

1-Phenyl-3,5-heptadiyne. A mixture of TMEDA (1.3 g, 11 mmol), cuprous chloride (1 g, 10 mmol), and acetone (10 ml) was thoroughly stirred in air and was transferred to a steel pressure reactor. Acetone (20 ml) and 1-phenyl-3-butyne (15 g, 0.115 mol) were added. The reactor was cooled to −78° and liquified methylacetylene (*ca.* 30 ml) was rapidly added. The reactor was sealed with a combination pressure gauge and gas-inlet valve. Upon warming to room temperature, the pressure rose to 60 psi. In order to add oxygen and concomitantly avoid its condensation, the reactor was cooled in liquid nitrogen and was then removed from the coolant, whereupon oxygen was added under pressure until the reactor pressure was 30 psi. The reactor was shaken and allowed to warm to room temperature, during which time the pressure in the

(50) Molecular weight determinations of phosphole sulfides and elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Unless specified otherwise, pmr spectra were recorded on a Varian A-60A or HA-100 spectrometer at ambient probe temperatures (*ca.* 45 or 30°, respectively) and refer to *ca.* 20% solutions in $CDCl_3$, with tetramethylsilane (TMS) as internal reference. Where appropriate, slow-exchange ($k < 0.1$ sec^{-1}) spectra were recorded at both 60 and 100 MHz to differentiate coupling constants from chemical shifts. Mass spectra were obtained on an AEI MS-9 high-resolution mass spectrometer. All reactions which involved the use of organometallic compounds as reagents or as intermediates were carried out under a high-purity nitrogen atmosphere so as to avoid oxidation and hydrolysis. All reactions involving phosphines were carried out under rigorous exclusion of oxygen, *i.e.*, under a high-purity nitrogen atmosphere and with solvents and reagents from which oxygen had been carefully removed.

(51) H. Taniguchi, I. M. Mathai, and S. I. Miller, *Tetrahedron*, 22, 867 (1966).

(52) A. S. Hay, *J. Org. Chem.*, 27, 3320 (1962).

reactor dropped from an initial value of 95 psi to a final value of *ca.* 45 psi. The above procedure of oxygen addition, followed by shaking and warming to room temperature, was continued over a period of 9 days, until a positive oxygen pressure remained after a prolonged period of time at room temperature. After unreacted gases were vented from the reactor, the reaction mixture was diluted with chloroform and washed with water until the aqueous washings were not green. The organic layer was concentrated at reduced pressure and the residual dark oil was chromatographed on silica gel, using 30–60° petroleum ether as eluent. Unreacted 1-phenyl-3-butyne was removed from the eluate at *ca.* 50° (0.1 mm). An attempt to isolate 1-phenyl-3,5-heptadiyne by high-vacuum fractional distillation of the residue was unsuccessful, since the heated material darkened and decomposed before any distillation occurred. Dark colored decomposition products were removed from this material by chromatography, as described above. The pmr spectra of the first few chromatography fractions were consistent with that expected for the desired product and featured a characteristic absorption at δ 1.85 (t, $^{7}J_{HH}$ = *ca.* 1 Hz) due to the methyl protons, in addition to absorptions at 2.28–3.19 (m, CH_2CH_2) and 7.22 (broadened s, C_6H_5). The high pmr integration values for the methylene and aromatic protons in this sample of the product, relative to the absorption at δ 1.85, were consistent with the presence of *ca.* 15% of 1,8-diphenyl-3,5-octadiyne, which is an expected contaminant produced by coupling of 1-phenyl-3-butyne with itself. The identity of 1-phenyl-3,5-heptadiyne was confirmed by mass spectral analysis. This sample was used in the preparation of 2-methyl-1-phenyl-5-(2-phenylethyl)phosphole (**2**) without further purification.

Synthesis of Phospholes by Cyclization of 1,3-Diynes and Phenylphosphine. General Method. The procedure for cyclization of 1,3-diynes of the type $R_1(C{\equiv}C)_2R_2$ with phenylphosphine was based on the method reported by Märkl and Potthast[9a] and is exemplified by the following preparation of **2-methyl-1,5-diphenylphosphole (1)**. A solution (4 ml; 1.6 *M*) of *n*-butyllithium in hexane was added dropwise to a cold (*ca.* 0°) solution of phenylphosphine (5.5 g, 50 mmol) in benzene (25 ml) and tetrahydrofuran (THF; 4 ml), which was magnetically stirred. To the resultant yellow solution 1-phenyl-1,3-pentadiyne (7 g, 50 mmol) was slowly added with stirring, during which time the color of the reaction mixture changed to dark red-purple. After complete addition, the reaction was stirred for 1 hr at 0°, and then overnight at room temperature. The reaction mixture was quenched with water (3 ml) and the separated organic layer was concentrated at reduced pressure on a rotary evaporator. The residue was kugelrohr distilled (120° (0.025 mm)) and gave the crude product (3.6 g, 30%) as a pale yellow solid. Sublimation (80° (0.1 mm)) of this material gave **1** as pale yellow needles, mp 84–87°. A molecular weight determination by the Signer method[53] (in acetone; triphenylphosphine standard; calcd: 250; found: 250) confirmed, as did mass spectral analysis, the assigned monomeric structure of **1**. The pmr spectrum of **1** showed absorptions at δ 2.09 (dd, $^{3}J_{PH}$ = 11.1 Hz, $^{4}J_{HH}$ = 1.7 Hz, CH_3), 6.62 (approximate doubled hextet, $^{3}J_{PH}$ = 12.5 Hz, $^{4}J_{HH}$ = 1.7 Hz, $^{3}J_{HH}$ = 3.3 Hz, 3-*H*), and 6.95–7.75 (m, aromatic and 4-*H*).

Sulfurization of **1** in the usual manner[54] gave **2-methyl-1,5-diphenylphosphole 1-sulfide** as yellow-green crystals: mp 93–94° (ether–pentane); mol wt (osmometry in benzene), calcd: 282; found: 287.

Anal. Calcd for $C_{17}H_{15}PS$: C, 72.32; H, 5.36; P, 10.97; S, 11.36. Found: C, 73.12; H, 5.33; P, 10.92; S, 9.91.

The pmr spectrum of this phosphole sulfide featured absorptions at δ 1.99 (dd, $^{3}J_{PH}$ = 13.1 Hz, $^{4}J_{HH}$ = 1.7 Hz, CH_3) and 6.70 (approximate doubled hextet, $^{3}J_{PH}$ = 38.9 Hz, $^{4}J_{HH}$ = 1.7 Hz, $^{3}J_{HH}$ = 3.6 Hz, 3-*H*).

2-Methyl-1-phenyl-5-(2-phenylethyl)phosphole (2). 1-Phenyl-3,5-heptadiyne, prepared as described above, was used for the reaction with phenylphosphine, and the cyclization procedure was analogous to that described above for the preparation of **1**. The crude product was purified by kugelrohr distillation (bp 155–160° (0.025 mm)) and gave **2** in 70% yield. The pmr spectrum (C_6D_6) of **2** was consistent with its assigned structure and showed absorptions at δ 2.00 (broadened d, $^{3}J_{PH}$ = 11.0 Hz, CH_3), 2.3–2.9 (m, CH_2CH_2), 6.44 (broadened d, $^{3}J_{PH}$ = 12.5 Hz, 3-*H* and 4-*H*), and 6.8–7.8 (m, aromatic).

Sulfurization of **2** in the usual manner[54] gave **2-methyl-1-phenyl-5-(2-phenylethyl)phosphole 1-sulfide** as a yellow liquid, which we were unable to crystallize. The pmr spectrum of this phosphole sulfide exhibited absorptions at δ 1.90 (dd, $^{3}J_{PH}$ = 13 Hz, $^{4}J_{HH}$ = 1 Hz, CH_3), 2.2–3.0 (m, CH_2CH_2), 6.50 (doubled multiplet, $^{3}J_{PH}$ = 39 Hz, 3-*H* and 4-*H*), and 6.9–8.0 (m, aromatic). The mass spectrum of this phosphole sulfide was also consistent with its assigned structure.

2-Isopropyl-1,5-diphenylphosphole (3). The method of preparation for **3** was essentially the same as that described above for **1**, except that a *ca.* 1:16 molar ratio of butyllithium:2-methyl-6-phenyl-3,5-hexadiyne was used. The crude product was isolated in 86% yield by kugelrohr distillation (bp 100–105° (0.025 mm)) as a bright yellow-green solid, which was purified by sublimation (95° (0.1 mm)) to give **3** as pale green needles, mp 73–76°. The pmr spectrum of **3** was consistent with its assigned structure and showed absorptions at δ 1.11 (d, $^{3}J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$), 2.4–2.9 (m, $CH(CH_3)_2$), 6.62 (dq, $^{3}J_{PH}$ = 12.2 Hz, $^{3}J_{HH}$ = 3.0 Hz, $^{4}J_{HH}$ = 1.4 Hz, 3-*H*), and 6.80–7.52 (m, aromatic and 4-*H*).

Sulfurization of **3** in the usual manner[54] gave **2-isopropyl-1,5-diphenylphosphole 1-sulfide** as yellow-green crystals: mp 96–103° (ether–pentane); mol wt (osmometry in benzene), calcd: 310; found: 298.

Anal. Calcd for $C_{19}H_{19}PS$: C, 73.52; H, 6.17; P, 9.98; S, 10.33. Found: C, 73.74; H, 6.17; P, 10.10; S, 10.27

The pmr spectrum of this phosphole sulfide featured doublets at δ 0.85 ($^{3}J_{HH}$ = 6.8 Hz) and 1.22 ($^{3}J_{HH}$ = 6.8 Hz), due to the diastereotopic isopropyl methyl protons, as well as an absorption at 6.72 (dq, $^{3}J_{PH}$ = 38.4 Hz, $^{3}J_{HH}$ = 3.8 Hz, $^{4}J_{HH}$ = 1.7 Hz, 3-*H*).

1-Isopropyl-2-methyl-5-(2-phenylethyl)phosphole (5). A solution of **2** (1.2 g, 5 mmol) in THF (5 ml) was added to a magnetically stirred suspension of lithium dispersion (84 mg, 12 mmol) in THF (15 ml) and the mixture was heated at 50–60° for 30 min. After additional stirring at room temperature for 12 hr, isopropyl bromide (1.2 ml, 13 mmol) was added to the purple reaction mixture, which was cooled in an ice bath, and the reaction mixture was then stirred at room temperature for 2 hr. Water (5 ml) was slowly added to decompose unreacted lithium, and the reaction mixture was then diluted with dichloromethane. The separated organic layer was concentrated at reduced pressure and the residual oil was kugelrohr distilled (bp 95–100° (0.03 mm)), yielding (60%) crude **5**. This distillate was purified by chromatography on Florisil, using pentane as eluent, and then by kugelrohr distillation of the eluate. The pmr spectrum ($CFCl_3$) of **5** showed absorptions at δ 1.12 (dd, $^{3}J_{PH}$ = 13.5 Hz, $^{3}J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$), 2.20 (broadened d, $^{3}J_{PH}$ = *ca.* 10 Hz, 2-CH_3), 1.6–2.4 (m, $CH(CH_3)_2$), 6.66 (broadened d, $^{3}J_{PH}$ = *ca.* 11 Hz, 3-*H* and 4-*H*), and 7.4 (broadened s, C_6H_5).

Sulfurization of **5** in the usual manner[54] gave **1-isopropyl-2-methyl-5-(2-phenylethyl)phosphole 1-sulfide** as a yellow-green oil, which we were unable to crystallize. The pmr spectrum of this phosphole sulfide was consistent with its assigned structure and featured absorptions at δ 1.13 (dd, $^{3}J_{PH}$ = 18.3 Hz, $^{3}J_{HH}$ = 7.0 Hz) due to the diastereotopic isopropyl methyl protons, and also showed absorptions at δ 2.05 (broadened d, $^{3}J_{PH}$ = *ca.* 12 Hz, 2-CH_3) and 6.46 (broadened d, $^{3}J_{PH}$ = *ca.* 36.5 Hz, 3-*H* and 4-*H*). Mass spectral analysis was also consistent with the assigned structure for this sulfide.

1-Isopropyl-2-methyl-5-phenylphosphole (4). The method for preparation of **4** was essentially the same as that described for **5**. The crude sample of **4**, which was isolated by kugelrohr distillation (bp 85–90° (0.04 mm)), was purified by chromatography on Florisil, using 30–60° petroleum ether as eluent, and was then redistilled (kugelrohr). The overall yield was 30%. The pmr spectrum of **4** ($CFCl_3$) showed absorptions at δ *ca.* 0.6–1.4 (broadened m, $CH(CH_3)_2$), 2.16 (dd, $^{3}J_{PH}$ = 10.0 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2-CH_3), 1.6–2.3 (m, $CH(CH_3)_2$), 6.54 (doubled sextet, $^{3}J_{PH}$ = 11.0 Hz, $^{3}J_{HH}$ = 3.0 Hz, $^{4}J_{HH}$ = 1.5 Hz, 3-*H*), 6.80 (dd, $^{3}J_{PH}$ = 9.5 Hz, $^{3}J_{HH}$ = 3.0 Hz, 4-*H*), and 6.9–7.6 (m, C_6H_5).

Sulfurization of **4** in the usual manner[54] gave **1-isopropyl-2-methyl-5-phenylphosphole 1-sulfide** as small pale green plates: mp 82.5–85.0° (ether–pentane); mol wt (osmometry in benzene), calcd: 248; found: 254.

Anal. Calcd for $C_{14}H_{17}PS$: C, 67.71; H, 6.90; P, 12.47; S, 12.91. Found: C, 67.69; H, 6.94; P, 12.27; S, 13.30.

The pmr spectrum of this phosphole sulfide featured absorptions at δ 1.02 (dd, $^{3}J_{PH}$ = 19.0 Hz, $^{3}J_{HH}$ = 7.0 Hz) and 1.18 (dd, $^{3}J_{PH}$ = 18.5 Hz, $^{3}J_{HH}$ = 7.0 Hz), due to the diastereotopic isopropyl methyl protons, as well as at δ 2.11 (dd, $^{3}J_{PH}$ = 12.0 Hz, $^{4}J_{HH}$ = 1.8 Hz, 2-CH_3), 6.59 (doubled hextet, $^{3}J_{PH}$ = *ca.* 35 Hz, $^{3}J_{HH}$ = 3.6 Hz, $^{4}J_{HH}$ = *ca.* 1.8 Hz, 3-*H*), 7.00 (dd, $^{3}J_{PH}$ = *ca.* 35 Hz, $^{3}J_{HH}$ = 3.6 Hz, 4-*H*), 7.23–7.48 (m, aromatic), and 7.80–7.98 (m, aromatic).

(53) A. Styermark in "Quantitative Organic Microanalysis," 2nd ed, Academic Press, New York, N. Y., 1961, p 535 ff.

(54) G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7023 (1969).

1-((*dl*)-2-Phenyl-2-methoxyethyl-*1*-d_2)-2-[illegible]phole (6). Cleavage of **1** with lithium and subsequent alkylation with (*dl*)-2-phenyl-2-methoxyethyl-*1*-d_2 bromide[12b] were carried out in the same manner as described above for the preparation of **5**. Kugelrohr distillation of the crude reaction product gave an initial fraction, bp *ca.* 40–100° (0.025 mm), which proved to be mainly unreacted bromide, and a second fraction, bp *ca.* 120–185° (0.025 mm), which consisted of a mixture of unreacted bromide and **6**. Slow kugelrohr distillation of the second fraction separated unreacted bromide, bp *ca.* 40–90° (0.025 mm), from **6**, bp 135–145° (0.025 mm), which was isolated in 22% yield. The mass and pmr spectra of **6** were consistent with its assigned structure. The pmr spectrum ($CFCl_3$) featured absorptions at δ 2.14 (dd, $^3J_{PH}$ = 11 Hz, $^4J_{HH}$ = *ca.* 1.5 Hz, 2-CH_3), 2.97 (s, OCH_3), 3.88 (broadened d, $^3J_{PH}$ = *ca.* 7.5 Hz, methine), 6.52 (approximate doubled hextet, $^3J_{PH}$ = 12 Hz, $^3J_{HH}$ = 3.0 Hz, $^4J_{HH}$ = *ca.* 1.5 Hz, 3-*H*), 6.89 (dd, $^3J_{PH}$ = 10 Hz, $^3J_{HH}$ = 3.0 Hz, 4-*H*), and 7.0–7.5 (m, aromatic). At −36°, the pmr spectrum ($CFCl_3$) of **6** indicated (by electronic integration) a 55:45 mixture of diastereomers. The predominant isomer featured characteristic absorptions at δ 2.07 (dd, $^3J_{PH}$ = 10.7 Hz, $^4J_{HH}$ = *ca.* 1.4 Hz, 2-CH_3), 2.99 (s, OCH_3), 3.97 (broadened d, $^3J_{PH}$ = 6.4 Hz, methine); the minor isomer featured characteristic absorptions at δ 2.20 (dd, $^3J_{PH}$ = 11.1 Hz, $^4J_{HH}$ = *ca.* 1.4 Hz, 2-CH_3), 2.95 (s, OCH_3), 3.73 (broadened d, $^3J_{PH}$ = 7.9 Hz, methine). The vinyl region indicated the presence of two diastereomers: the 3-*H* proton was centered at *ca.* δ 6.62 and appeared as a broadened approximately doubled octet (overlapping doubled sextets); the 4-*H* proton was centered at *ca.* δ 6.92 and appeared as doubled quartets (overlapping doubled doublets).

3-*n*-Butyl-1-((*dl*)-2-phenyl-2-methoxyethyl-*1*-d_2)-2-phenylphosphindole (8). A solution of diphenylacetylene (1.78 g, 10 mmol) in THF (10 ml), which was cooled by a water–ice bath, was treated with a hexane solution of *n*-butyllithium (12.5 ml; *ca.* 1.6 *M*) and the dark red reaction mixture was then stirred at room temperature for 16 hr. A solution of phenylphosphonous dichloride (1.35 ml, 10 mmol) in THF (5 ml) was added to the stirred and cooled reaction mixture, which was then refluxed for 6 hr and then stirred at room temperature for 12 hr. After hydrolysis with water (5 ml) and removal of THF at reduced pressure, dichloromethane (10 ml) was added and the separated organic layer was washed with water (10 ml). Removal of dichloromethane yielded a viscous dark oil, which was kugelrohr distilled to give a thick pale yellow oil, bp 135–210° (*ca.* 0.09 mm), whose pmr spectrum was consistent with that expected for the reported[55] product of this reaction, 3-*n*-butyl-1,2-diphenylphosphindole (**7**) (1.55 g, 45%). A solution of **7** (1.05 g, 3.1 mmol) in THF (10 ml) was refluxed with lithium dispersion (45 mg, 6.4 mmol) for 3 hr. Racemic 2-phenyl-2-methoxyethyl-*1*-d_2 bromide[12b] (1.33 g, 6.1 mmol) was added to the cooled reaction mixture, which was refluxed for 2 hr and then stirred at room temperature for 12 hr. After hydrolysis and work-up of the reaction mixture, as described above for **6**, the crude product, **8**, was collected by kugelrohr distillation as a thick yellow oil (0.76 g, 62%), bp 160–210° (0.03 mm). Chromatography of crude **8** on Florisil, using 1:1 benzene–petroleum ether (30–60°) as eluent, gave **8** (*ca.* 0.5 g). The pmr spectrum of **8** (benzonitrile; hexamethyldisilane, internal reference) was consistent with its assigned structure and indicated (by electronic integration) a *ca.* 56:44 mixture of diastereomers. The predominant isomer featured absorptions at δ 2.95 (s, OCH_3) and 4.05 (broadened d, $^3J_{PH}$ = *ca.* 7 Hz, methine), and the minor isomer featured similar absorption patterns for the corresponding diastereotopic nuclei at δ 2.84 and 4.10, respectively.

Hydrogen peroxide oxidation of **8**, in the usual manner,[56] gave **3-*n*-butyl-1-((*dl*)-2-phenyl-2-methoxyethyl-*1*-d_2)-2-phenylphosphindole 1-oxide** which was purified by kugelrohr distillation (bp 210–230° (0.07 mm)) and isolated as a colorless viscous oil. The pmr spectrum of this oxide was consistent with its assigned structure and indicated (by electronic integration) a *ca.* 56:44 mixture of diastereomers. The predominant isomer featured absorptions at δ 3.25 (s, OCH_3) and 4.68 (broadened d, $^3J_{PH}$ = *ca.* 8.5 Hz, methine), and the minor isomer featured similar absorption patterns for the corresponding diastereotopic nuclei at δ 2.70 and 4.38, respectively. The mass spectrum of this oxide was likewise consistent with its assigned structure.

3-Methyl-5-phenyldibenzophosphole (9). According to the procedure of Hellwinkel,[57] isoamyl nitrite (67 ml, 0.5 mol) was added to a solution of 2-bromo-4-methylaniline[58] (86 g, 0.46 mol) in benzene (275 ml, 3.1 mol) and the resultant exothermic reaction maintained self-reflux for *ca.* 30 min. The reaction mixture was refluxed for an additional 12 hr and was cooled to room temperature, diluted with benzene (300 ml), and then washed twice with 250-ml portions of water. The organic layer was dried (magnesium sulfate) and then treated with activated charcoal. After filtration, removal of solvent at reduced pressure gave a dark red residue, which was chromatographed on silica gel (*ca.* 500 g), using hexane eluent. The eluate was kugelrohr distilled to give the crude product as a bright yellow oil (15 g), bp *ca.* 90–105° (0.1 mm). Rechromatography as above, followed by kugelrohr distillation of the eluate, yielded 2-bromo-4-methylbiphenyl as a pale yellow oil (12.5 g, 11%), bp *ca.* 80–90° (0.3 mm) (lit.[59] bp 301–303°). Conversion of this compound to 4-methyl-2-biphenylylphenylphosphinic acid (48% yield) was carried out according to the procedure of Campbell and Way,[60] except that 4-methyl-2-biphenylylmagnesium iodide was replaced with the corresponding organolithium derivative, prepared by refluxing a solution of 2-bromo-4-methylbiphenyl (8.3 g, 33.6 mmol) in hexane (50 ml) with 1 equiv of *n*-butyllithium for 16 hr. Crude 4-methyl-2-biphenylylphosphinic acid was used for cyclization to 3-methyl-5-phenyldibenzophosphole 5-oxide by reaction with phosphorus pentachloride in nitrobenzene;[60] a modified work-up procedure was used as follows. The cooled reaction mixture was cautiously hydrolyzed with 15% aqueous sodium hydroxide and then extracted with chloroform. The organic layer was washed with water, dried (magnesium sulfate), concentrated on a rotary evaporator, and then chromatographed on silica gel, eluting first with benzene to remove nitrobenzene and then with chloroform. A portion of the viscous dark eluate was kugelrohr distilled (bp 220–230° (0.1 mm)). Repeated crystallization from ethyl acetate–hexane gave 3-methyl-5-phenyldibenzophosphole 5-oxide as a white powder, mp 135–140° (lit.[60] mp 146–147°). The pmr spectrum of this oxide was consistent with its assigned structure and featured a broadened singlet at δ 2.35, due to the ring methyl protons; relatively weak singlet absorptions at δ 2.18 and 4.62 indicated some contamination.

A solution of crude 3-methyl-5-phenyldibenzophosphole 5-oxide (*ca.* 4 g, 14 mmol) in phenylsilane[61] (*ca.* 5 ml, 40 mmol) was heated at 60–70° for 1 hr and then allowed to stand at room temperature for 12 hr. Unreacted phenylsilane was removed at room temperature under reduced pressure, and the dark residue was kugelrohr distilled to give **9** (*ca.* 3 g, 80%) as a thick colorless oil, bp 130–150° (0.05 mm). The pmr spectrum (C_6D_6) of **9** showed absorptions at δ 2.07 (broadened s, CH_3) and 6.8–7.8 (m, aromatic).

5-((*dl*)-2-Phenyl-2-methoxyethyl-*1*-d_2)-3-methyldibenzophosphole (10). The following preparation was based by analogy on a report by Ezzell and Freedman.[62] A solution of **9** (1.75 g, 6.4 mmol) in THF (17.5 ml) was refluxed with lithium dispersion (100 mg, 14 mmol) for 3 hr and was cooled to room temperature. The dark red reaction mixture was treated with *tert*-butyl chloride (0.7 ml, 6.4 mmol) and refluxed for 10 min. Racemic 2-phenyl-2-methoxyethyl-*1*-d_2 bromide[12b] (1.4 g, 6.4 mmol) was added to the cooled reaction mixture and the resultant light green solution was refluxed for 15 min. After hydrolysis with water (5 ml) and removal of THF on a rotary evaporator, the residue was extracted with benzene (20 ml) and the separated organic layer was washed twice with water (5 ml). The organic layer was concentrated on a rotary evaporator and unreacted (*dl*)-2-phenyl-2-methoxyethyl-*1*-d_2 bromide was removed from the residue by kugelrohr distillation, as described above in the preparation of **6**. The residue was oxidized with 30% aqueous hydrogen peroxide in the usual manner[56] to give **5-((*dl*)-2-phenyl-2-methoxyethyl-*1*-d_2)-3-methyldibenzophosphole 5-oxide (17)**, which was then chromatographed on silica gel, eluting first with benzene and then with benzene which contained gradually increasing percentages of chloroform. Pmr analysis of the first few chromatography fractions containing **17** indicated (by electronic integration) a *ca.* 65:35 mixture of diastereomers **17a–17b**. Isomer **17a**

(55) M. D. Rausch and L. P. Klemann, *J. Amer. Chem. Soc.*, **89**, 5732 (1967).
(56) K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7012 (1969).
(57) D. Hellwinkel, *Chem. Ber.*, **99**, 3642 (1966).
(58) Prepared by the method of J. R. Johnson and L. T. Sandborn, "Organic Syntheses," Collect. Vol. I, 2nd ed, Wiley, New York, N. Y., 1967, p 111.
(59) M. Gomberg and J. C. Pernert, *J. Amer. Chem. Soc.*, **48**, 1372 (1926).
(60) I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 2133 (1961).
(61) Prepared by the method of R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Amer. Chem. Soc.*, **74**, 648 (1952).
(62) B. R. Ezzell and L. D. Freedman, *J. Org. Chem.*, **34**, 1777 (1969).

featured absorptions at δ 2.34 (broadened s, 3-CH_3), 3.24 (s, OCH_3), and 4.88 (d, $^3J_{PH}$ = 8.5 Hz, methine); isomer **17b** featured similar absorption patterns for the corresponding diastereotopic nuclei at δ 2.41, 3.24, and 4.83, respectively. Pmr analysis of the last few chromatography fractions containing **17** indicated a *ca.* 35:65 mixture of **17a–17b**. The combined middle chromatography fractions (1.35 g), which contained the bulk of **17** (1.5 g, 67% yield), were crystallized from benzene–hexane and yielded crystals having two distinct crystalline habits (colorless clusters and small white needles), which were manually separated. Pmr analysis of the colorless clusters (0.8 g) and of the small white needles (0.2 g, mp 118–120°) indicated that they were 44:56 and 72:28 mixtures of **17a–17b**, respectively. Slow recrystallization of the colorless clusters from benzene–hexane gave colorless rhomboidal plates (mp 131–136°), which were a 36:64 mixture of **17a–17b**. Further attempts to increase diastereomeric enrichment by fractional recrystallization from benzene–hexane were unsuccessful. Mass spectral analysis: isotopic abundance calcd for **17** ($C_{22}H_{19}D_2PO_2$): $(M+1)^+/M^+$ = 24.78%, $(M+2)^+/M^+$ = 3.39%. Found: $(M+1)^+/M^+ = 23.85 \pm 0.37\%$, $(M+2)^+/M^+ = 2.94 \pm 0.37\%$.

Reduction of **17** to **10** was accomplished by heating a 39:61 mixture of **17a–17b** (300 mg, 0.85 mmol) with phenylsilane[61] (6 ml, 48 mmol) for 10 min at 60°. Unreacted phenylsilane was removed under high vacuum and the viscous residue was dissolved in benzene (5 ml) and treated with 30% aqueous sodium hydroxide (1 ml). The mixture was stirred at room temperature for 15 min, water (5 ml) was added, and the separated organic layer was chromatographed on silica gel using benzene as eluent. The product, **10**, was obtained as a viscous oil (*ca.* 100 mg, 34%). The pmr spectrum of this oil was consistent with that expected for a diastereomerically enriched mixture of **10** and featured absorptions at δ 4.39 (broadened d, $^3J_{PH}$ = *ca.* 7.5 Hz) and 4.35 (broadened d, $^3J_{PH}$ = *ca.* 7.5 Hz), due to the methine protons in the minor (**10a**) and major (**10b**) isomers, respectively; comparison of the relative peak heights of these signals indicated a *ca.* 40:60 mixture of **10a–10b**. Oxidation of an aliquot of this sample of **10** with hydrogen peroxide, in the usual manner,[56] gave a 39:61 mixture of **17a–17b**. Phenylsilane reduction of a 65:35 mixture of **17a–17b** at 65° for 50 min yielded a 60:40 mixture of **10a–10b**.

Methyl 2-(*o*-bromophenyl)propyl Ether. A solution of methyl *o*-bromobenzoate[63] (53.3 g, 0.25 mol) in ether (250 ml) was added dropwise to a mechanically stirred solution of methylmagnesium iodide (0.59 mol) in ether (335 ml). After complete addition, the mixture was stirred for *ca.* 30 min and was then hydrolyzed with 5% aqueous hydrochloric acid (800 ml). The separated organic layer was dried (magnesium sulfate) and was concentrated on a rotary evaporator to give the crude product, which was purified by distillation to yield (79%) **2-(*o*-bromophenyl)propan-2-ol**,[64] bp 78° (0.3 mm). The pmr spectrum of this compound was consistent with that expected and featured absorptions at δ 1.75 (s, C(CH_3)$_2$) and 2.94 (s, OH).

A solution of 2-(*o*-bromophenyl)propan-2-ol (139 g, 0.65 mol) and aqueous 48% hydrobromic acid (1 l.) was heated on a steam bath for 1 hr. Dimethylformamide (DMF; 2.2 l.) was added and the mixture was stirred overnight at room temperature. The reaction mixture was diluted with water, extracted with pentane, and the combined organic layers were washed with water, dried (magnesium sulfate), and then concentrated on a rotary evaporator. The residue was purified by distillation to yield (85%) α-methyl-*o*-bromostyrene,[64] bp 55–65° (*ca.* 2 mm) (lit.[65] bp 80° (1 mm)). Identification of this compound was based on its mass and pmr spectra: pmr δ 2.08 (m, CH_3), 4.96 (m, 1 vinyl H), 5.24 (m, 1 vinyl H), and 6.9–7.7 (m, aromatic).

Hydroboration–oxidation of α-methyl-*o*-bromostyrene (60.5 g, 0.307 mol) with lithium borohydride–boron trifluoride etherate was carried out according to the procedure of Brown and Zweifel,[66] using a stoichiometry of olefin–lithium borohydride–boron trifluoride = 6.0:3.0:1.0 (*i.e.*, twice the theoretical[67] amount of hydroborating reagents needed), to ensure complete hydroboration. The crude product was purified by distillation and yielded a thick colorless oil (54 g, 82%), bp 93–97° (0.1 mm), which was identified as the expected[67] product, **2-(*o*-bromophenyl)propan-1-ol**, on the basis of its characteristic pmr spectrum: δ 1.27 (d, $^3J_{HH}$ = 6.5 Hz, CH_3), 1.88 (s, OH), 3.2–4.1 (m, CHCH_2), and 6.9–7.7 (m, aromatic). The high stereospecificity of this hydroboration was evidenced by the fact that this product contained only *ca.* 1% of the 2-(*o*-bromophenyl)-propan-2-ol isomer, as indicated by the relative integrated intensities of the characteristic pmr signals due to the methyl protons in each isomer at δ 1.27 and 1.75, respectively.

A solution of 2-(*o*-bromophenyl)propan-1-ol (27.8 g, 0.13 mol) in anhydrous DMF (50 ml) was added dropwise to a magnetically stirred suspension of sodium hydride (*caution:* hydrogen evolution) in anhydrous DMF (70 ml) and methyl iodide (16 ml, 0.26 mol), which was cooled with a water bath. After complete addition, the reaction mixture was stirred at room temperature for 24 hr. Unreacted sodium hydride was decomposed by cautious addition of water (250 ml) and the product was extracted with two 250-ml portions of pentane. The combined pentane extracts were washed with two 250-ml portions of water, dried (magnesium sulfate), and then concentrated on a rotary evaporator. The light yellow residual oil was purified by distillation and yielded (59%) methyl 2-(*o*-bromophenyl)propyl ether, bp 56–60° (0.25 mm). The mass spectrum of this material was consistent with its assigned structure and the pmr spectrum featured absorptions at δ 1.32 (broadened d, $^3J_{HH}$ = *ca.* 6.5 Hz, CHCH_3), 3.45 (s, OCH_3), and 3.6–3.9 (m, CHCH_2). Conversion of this compound to **13** (see below) confirmed the assigned structure.

1-Benzyl-3-methyl-1-phenylphosphindolinium Bromide (13). A solution of 1,2-dibromoethane (66 g, 0.35 mol) in ether (350 ml) was added dropwise, over a period of 6 hr, to a vigorously stirred suspension of magnesium turnings (30.8 g, 1.27 mol) in a solution of methyl 2-(*o*-bromophenyl)propyl ether (16.1 g, 70 mmol) in ether (150 ml). After complete addition, the mixture was stirred and refluxed for 3 hr and then a solution of benzylphenylphosphinyl chloride[68] (15 g, 60 mmol) in benzene (125 ml) was added dropwise to the stirred and refluxing reaction mixture. After continued stirring at room temperature for 12 hr, ether was then removed by distillation, while benzene was added, until the reflux temperature increased to approximately 80°. Reflux was continued for 2 hr and the reaction mixture was then hydrolyzed by addition of saturated aqueous ammonium chloride solution (150 ml), and then 15% aqueous hydrogen chloride (200 ml). After stirring at room temperature for 12 hr, the reaction mixture was diluted with benzene and enough water and 15% aqueous hydrogen chloride were then added to dissolve the magnesium salts. The separated aqueous layer was extracted with an equal volume of chloroform and the combined organic layers were dried (magnesium sulfate) and then concentrated on a rotary evaporator. The residue was kugelrohr distilled to yield a thick oil, bp 170–200° (0.03 mm), whose pmr spectrum was consistent with that expected for an approximately equimolar mixture of the diastereomers of **benzylphenyl[*o*-(1-methyl-2-methoxyethyl)-phenyl]phosphine oxide (11)**; diastereotopic *C*-methyl protons gave rise to doublets ($^3J_{HH}$ = 6.5 Hz) at δ 0.88 and 1.08, and diastereotopic *O*-methyl protons exhibited singlets at δ 2.92 and 3.23.

Reduction of this sample of **11**, in the usual manner,[56] with hexachlorodisilane in refluxing benzene for 2 hr yielded (81%) **benzylphenyl[*o*-(1-methyl-2-methoxyethyl)phenyl]phosphine (12)**, which was kugelrohr distilled, bp 130–150° (0.05 mm). The pmr spectrum of **12** was consistent with its assigned structure and featured singlets of approximately equal intensity at δ 3.05 and 3.18, due to the diastereotopic *O*-methyl protons.

The following procedure for cyclization of **12** to **13** is a modification of the method reported by Mann and Millar.[13] Anhydrous hydrogen bromide was bubbled into a refluxing solution of **12** (10.0 g, 29 mmol) in glacial acetic acid (150 ml) and aqueous 48% hydrogen bromide (150 ml) for 3 hr. Most of the acetic acid, hydrogen bromide, and water were removed *in vacuo* (water aspirator, *ca.* 20 mm) and the residue was treated with water (200 ml), made basic by addition of sodium bicarbonate, and then rapidly diluted with chloroform (400 ml). After the mixture was stirred for 5 min, the chloroform layer was separated and then dried (magnesium sulfate). The filtered chloroform solution was refluxed for 5 hr and then concentrated to a volume of *ca.* 50 ml on a rotary evaporator. Crystallization was induced by addition of ether, and, after 2 days at 0°, **13** (3.7 g, 32%) was isolated as a white crystalline solid, mp 230–240°. The pmr spectrum (trifluoroacetic acid) of **13** indicated an approximately equimolar mixture of the diastereomers and

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(64) We thank Dr. P. O. Crews for this preparation.
(65) E. A. Khrustaleva, M. A. Bulatov, and S. S. Spasskii, *Tr. Inst. Khim., Akad. Nauk SSSR, Ural. Filial*, No. 13, 13 (1966); *Chem. Abstr.*, **68**, 87339t (1968).
(66) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **82**, 4708 (1960).
(67) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 26 (1963).
(68) Prepared by the method of T. L. Emmick and R. L. Letsinger, *J. Amer. Chem. Soc.*, **90**, 3459 (1968).

featured absorptions due to the diastereotopic methyl protons at δ 1.20 (dd, $^3J_{HH}$ = 7.0 Hz, $^4J_{PH}$ = *ca.* 1 Hz) and 1.43 (dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{PH}$ = *ca.* 1 Hz), and absorptions due to the diastereotopic (by external comparison) benzylic protons at δ 4.34 (d, $^2J_{PH}$ = 15 Hz) and 4.38 (m). Fractional recrystallization of this sample of **13** from 95% ethanol gave a sample in which the diastereomeric ratio was 2:1, with the predominant isomer giving rise to the lower field (in $CDCl_3$) pmr absorption for the methyl protons. This mixture was crystallized from chloroform (to remove entrained ethanol) to give a sample of **13**, mp 240–243°.

Anal. Calcd for $C_{22}H_{22}PBr$: C, 66.51; H, 5.58; P, 7.80; Br, 20.11. Found: C, 66.41; H, 6.11; P, 7.84; Br, 20.10.

3-Methyl-1-phenylphosphindoline 1-Oxide (14). A solution of **13** (1.6 g, 4 mmol; diastereomeric ratio = *ca.* 1:1) in 1 *N* aqueous sodium hydroxide (50 ml) was refluxed for 12 hr and the product was then extracted by washing the reaction mixture four times with 100-ml portions of dichloromethane. The combined organic layers were washed with saturated aqueous sodium chloride solution, dried (magnesium sulfate), and concentrated on a rotary evaporator. The residue was kugelrohr distilled to give **14** (0.85 g, 87%), bp 160–170° (0.05 mm), which was chromatographed on silica gel. Elution was begun with benzene and was continued with benzene containing increasing proportions of chloroform. The first few, and last few, chromatography fractions containing **14** were found by pmr analysis to be diastereomerically homogeneous (>*ca.* 95%) and were each purified by sublimation (100–110° (0.1 mm)) to give samples of **14a** (250 mg, mp 94–97°) and **14b** (100 mg, mp 87–96°), respectively. The pmr spectrum of **14a** showed absorptions at δ 1.53 (dd, $^3J_{HH}$ = 7.0 Hz, $^4J_{PH}$ = *ca.* 1 Hz, CH_3), 1.7–2.9 (m, CH_2), 3.1–3.6 (m, C*H*), and 7.1–7.9 (m, aromatic). The pmr spectrum of **14b** was similar to that of **14a** and featured characteristic absorptions at δ 1.45 (dd, $^3J_{HH}$ = 7.0 Hz, $^4J_{PH}$ = *ca.* 1 Hz, CH_3) and 3.4–4.1 (m, C*H*). Except for relative ion intensities, the mass spectra of **14a** and **14b** were similar; the most abundant peaks were at *m/e* 242 (M^+) and 227 ($(M - 15)^+$). A sample of **14a** was submitted for elemental analysis.

Anal. Calcd for $C_{15}H_{15}PO$: C, 74.37; H, 6.24; P, 12.79. Found: C, 74.38; H, 6.25; P, 12.86.

3-Methyl-1-phenylphosphindoline (15). A 25:75 mixture of **14a–14b** (220 mg, 0.9 mmol) was heated in phenylsilane[61] (0.25 ml, 2 mmol) at 70–75° for 20 min and then allowed to stand at room temperature for 45 min. Unreacted phenylsilane was removed under vacuum at room temperature and the residue was kugelrohr distilled to give an approximately quantitative yield of **15**, bp 80–90° (0.05 mm). The pmr spectrum (C_6D_6) of **15** was consistent with its assigned structure and featured characteristic doublets ($^3J_{HH}$ = 7.0 Hz) for the diastereotopic methyl protons of **15a** and **15b** at δ 1.05 and 1.08, respectively. The relative integrated intensities of these signals were measured with a Du Pont Model 310 curve resolver and indicated a 72:28 mixture of **15a–15b**.

3-Methyl-1-phenylphospholane 1-Oxide (18). A mixture of Raney nickel (1 teaspoonful; washed several times with absolute ethanol to remove water) and 3-methyl-1-phenyl-2-phospholene 1-oxide[69] (20 g, 0.1 mol) in absolute ethanol (250 ml) was hydrogenated in a Parr bomb at 50 psi for 10 hr. After removal of catalyst by filtration, solvent was removed on a rotary evaporator and the residue was kugelrohr distilled, to give **18** (20 g), bp 120° (0.025 mm). The pmr spectrum (C_6D_6) of this sample was consistent with its assigned structure and indicated the presence of one diastereomer, **18a**, which showed absorptions at δ 0.88 (dd, $^3J_{HH}$ = *ca.* 6 Hz, $^4J_{PH}$ = *ca.* 1 Hz, CH_3), *ca.* 1.0–2.6 (m, ring protons), and *ca.* 7.2–8.2 (m, C_6H_5). A mixture of **18a** and its diastereomer, **18b**, was obtained by stirring **18a** (100 mg) with N_2O_4 (*ca.* 1 ml) at 0° for 1 hr.[14] The pmr spectrum (C_6D_6) of this isomeric mixture, which was enriched in **18a**, indicated that the ring methyl protons of **18b** absorb at slightly lower field (*ca.* 2 Hz at 60 MHz) than those of **18a** and appear as shoulder absorptions ($^4J_{PH}$ = *ca.* 1 Hz) on the latter signals. The chemical shifts of these methyl protons were found to be concentration dependent in C_6D_6, and the above resonances refer to 2.8 *M* solutions.

Quantitative estimates of the diastereomeric purity of **18** were obtained by pmr analysis of **19**, which was synthesized by stereospecific reduction of **18** to 3-methyl-1-phenylphospholane (**16**) with phenylsilane, and subsequent quaternization of **16** with methylene iodide to give 1-iodomethyl-3-methyl-1-phenylphospholanium iodide (**19**) (see below).[14] Use of this analytical procedure to determine the diastereomeric purity of the sample of **18a** prepared above indicated that it was a 90:10 mixture of **18a–18b**.

3-Methyl-1-phenylphospholane (16). A sample of **18** was reduced with phenylsilane as described for the reduction of **14**. Kugelrohr distillation of the crude reaction product gave **16**, bp 55–85° (0.05 mm), in 74% yield. The pmr spectrum (C_6D_6) of **16** was consistent with its assigned structure and showed absorptions at δ 0.92 (broadened d, $^3J_{HH}$ = *ca.* 5 Hz, CH_3), *ca.* 1.0–2.7 (m, ring protons), and *ca.* 7.1–7.6 (m, C_6H_5). Treatment of the distillate with a fivefold molar excess of methylene iodide in benzene on standing at room temperature gave a white precipitate. The mixture was heated at *ca.* 55° for 1 hr. Addition of ether caused complete precipitation of the product, **1-iodomethyl-3-methyl-1-phenylphospholanium iodide (19).** The pmr spectrum (trifluoroacetic acid) of this sample of **19** was consistent with its assigned structure and featured doublets ($^2J_{PH}$ = 8 Hz) due to the iodomethyl protons in **19a** and **19b** at δ 3.98 and 4.01, respectively. Integration of these signals using a Du Pont Model 310 curve resolver indicated a 90:10 mixture of **19a–19b**. Thus, the sample of **16** prepared above was a 90:10 mixture of **16a** and **16b**. An isomeric mixture of **19**, which was obtained from a 60:40 mixture of **16**, was submitted for elemental analysis.

Anal. Calcd for $C_{12}H_{17}PI_2$: C, 32.31; H, 3.84; P, 6.94; I, 56.90. Found: C, 32.01; H, 3.99; P, 6.91; I, 57.18.

Dnmr Measurements. Pmr spectra were recorded on a Varian A-60A or a Varian HA-100 spectrometer equipped with variable-temperature accessories. Temperature measurements were based on the chemical-shift separation of the protons of an ethylene glycol sample or of a methanol sample, which contained a trace of hydrochloric acid, and utilized the temperature-shift correlation of Van Geet.[70] Temperatures are believed to be accurate to ±2°, although within a given series of measurements smaller differences (*ca.* ±0.5°) are considered significant. Spectra for line-shape analysis were recorded at 100 MHz while other dnmr spectra were recorded at 60 MHz. Sweep widths of 50 or 100 Hz and sweep times of 250 (at 60 MHz) or 500 (at 100 MHz) sec were used. Saturation of the pmr signals was avoided. The A-60A spectra were calibrated by the modulation side-band technique, using a Hewlett-Packard 200CD wide-range oscillator and a Hewlett-Packard 5212A electronic counter. The HA-100 spectra were calibrated using the difference frequency between the lock signal and pen position (DIFF 1 of the signal monitor) as measured on the V-4315 signal counter. Dnmr samples were *ca.* 25% v/v solutions with *ca.* 5% v/v TMS or hexamethyldisilane (for temperatures in the 75–200° range) and *ca.* 5% v/v methylene chloride (internal homogeneity reference). Either TMS or hexamethyldisilane was used as the lock signal for the 100-MHz (frequency sweep mode) spectra. Dnmr samples were sealed under vacuum in precision thin-wall nmr tubes.

The line-shape analyses were performed on an IBM 360/91 computer equipped with a Calcomp plotting accessory.

Equilibration Rate Measurements. Compound 10. A solution of a *ca.* 40:60 mixture of **10a–10b** (*ca.* 100 mg, 0.3 mmol) in benzene (10 ml), which was contained in a tube fitted with a rubber septum cap, was placed in a Neslab constant temperature circulating oil bath preset and maintained at 59.8 ± 0.05°. An aliquot (2.5 ml) of **10** was removed by syringe after 5, 35, 95, and 210 min. Each aliquot was rapidly injected into a magnetically stirred 0.18 *M* aqueous hydrogen peroxide solution (5 ml; *ca.* tenfold molar excess hydrogen peroxide) cooled to ice-bath temperature, and after a few minutes the heterogeneous reaction mixture was vigorously stirred at room temperature for 1.5–2 hr. Work-up for each oxidized aliquot was the same: water (10 ml) was added and **17** was extracted with three 10-ml portions of benzene. The combined organic layers were dried (magnesium sulfate) and concentrated on a rotary evaporator, and the residue was analyzed by pmr to obtain the ratio of **17a–17b**, using the relative peak heights of their characteristic ring methyl proton signals (see above). For each oxidized aliquot, the ratio of **17a–17b** (average of five scans) was set equal to the ratio of **10a–10b** at the time when the aliquot was removed from the heating bath. This same oxidation procedure and analytical method were used on a separately prepared sample of **10** in benzene, which had been heated at 59.8 ± 0.05° for 48 hr, and indicated that the equilibrium mixture of **10a–10b** at this temperature was 51.2:48.8. A least-squares treatment (correlation coefficient 0.997) of $\ln[(R - K)/(1 + R)]$ *vs.* *t* (eq 3) using the four data points and the value of *K*, together with the Eyring equation,[18] gave the values of $\Delta G^{\ddagger}$ for **10** reported in Table I.

(69) L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, **33**, 1034 (1968).

(70) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970); **40**, 2227 (1968).

Compound 15. A C_6D_6 solution of a 72:28 mixture of **15a–15b** was prepared, as described above, and was degassed and sealed in an nmr tube. The sample was placed in a high-temperature Colora Ultra Thermostat circulating oil bath preset and maintained at 130.0 ± 0.5° and it was removed periodically and rapidly cooled in an ice bath. The ratio of **15a–15b** was measured by pmr (at *ca.* 40°), using the relative absorption intensities of the ring methyl protons. Because of the small chemical-shift difference between these characteristic signals, direct electronic integration was not feasible, and therefore relative peak heights were used as a measure of **15a–15b**. Comparison of a few of these isomeric ratios with corresponding values obtained using a Du Pont Model 310 curve resolver verified the accuracy of the relative peak height method. After 26 days at 130.0°, the equilibrium mixture of **15a–15b** was 37.9:62.1. A least-squares treatment (correlation coefficient 0.999) of $\ln [(R - K)/(1 + R)]$ *vs.* t (eq 3) using ten data points, collected over a period of *ca.* 11 days, together with the value of K and the Eyring equation,[18] gave the values of $\Delta G^{\pm}$ for **15** reported in Table I.

Compound 16. A 90:10 mixture of **16a–16b** (160 mg) was prepared as described above and was dissolved in benzene (4 ml). Four 1-ml aliquots of this solution were placed in micro-Carius tubes and were degassed and sealed. The tubes were placed in a high-temperature Colora Ultra Thermostat circulating oil bath preset and maintained at 170.0 ± 0.5° and one tube was removed (quenched in ice–water bath) after 1, 8, 21, and 99 hr. Each tube was opened in a glove bag and methylene iodide (1 ml; *ca.* 50-fold molar excess) was then added. After 1–2 hr at *ca.* 50°, the four samples of **19** were isolated in essentially quantitative yield by precipitation with ether and were analyzed by pmr for purity and diastereomeric composition (with a Du Pont Model 310 curve resolver), using the characteristic signals of the iodomethyl protons for **19a** and **19b** (see above). The isomeric mixtures of **19**, which were derived from the aliquots removed after 21 and 99 hr, were the same (within experimental error) and gave an average value of 44:56 for **19a–19b**. Since the quaternization of **16** with methylene iodide to give **19** is stereospecific,[14] the equilibrium mixture of **16** was a 44:56 mixture of **16a–16b**. Setting the ratio of **16a–16b** at t_0 equal to 90:10 (see above), a least-squares treatment (correlation coefficient 0.996) of $\ln [(R - K)/(1 + R)]$ *vs.* t (eq 3) using three data points, together with the value of K and the Eyring equation,[1] gave the values for $\Delta G^{\pm}$ for **16** reported in Table I.

The Chlorinolysis of Medium-Ring Cycloalkyl 2,4-Dinitrobenzenesulfenates in Acetic Acid. Transannular Hydride Shifts[1]

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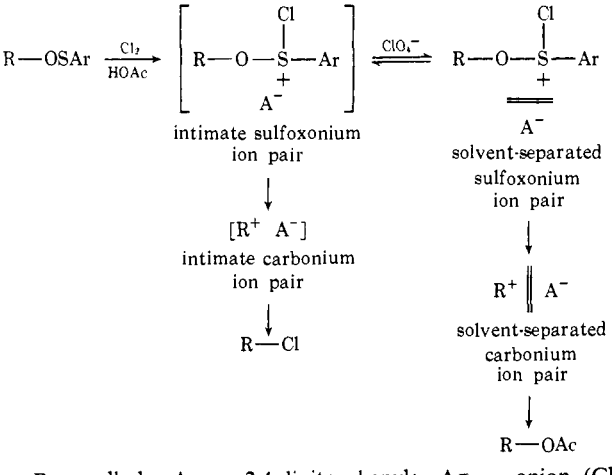
Abstract: A study of the chlorinolysis of deuterium-labeled cycloalkyl 2,4-dinitrobenzenesulfenates (ring sizes 8 and 10) in acetic acid has made possible the comparison of transannular hydride shifts occurring in different intermediate ion pairs. The dependence of product distributions on added lithium perchlorate has led to the conclusion that chloride product arises from intimate ion pairs and acetate from solvent-separated ones. The deuterium scrambling in the products implies that transannular hydride shifts occur to nearly the same extent in both ion pair species.

The chlorinolysis of alkyl 2,4-dinitrobenzenesulfenates in acetic acid has provided useful information on the mechanistic studies of ionic reactions, as extensive characterization of ion pairing behavior has been made in a number of systems.[3] Generally, the arenesulfenate is chlorinated to form an intimate sulfoxonium ion pair which may lose a sulfinyl chloride fragment, before or after solvent reorganization, to form the corresponding carbonium ion pair. These carbonium ions (which form chloride, acetate, and olefin products) are "born in an inherited solvent environment"[3b] (see Scheme I). It has been shown that the chloride–acetate ratio decreases sharply in the presence of added lithium perchlorate,[3] a manifestation of a "special salt effect."[4] Since perchlorate anion has the

Scheme I[a]



[a] R = alkyl; Ar = 2,4-dinitrophenyl; A^- = anion (Cl^-, AcO^-, ClO_4^-), not necessarily identical at each appearance in the scheme.

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