of the methoxyl groups, as evidenced in the nmr spectra, occurs at an even lower temperature in **6** and in **9** than in **1** and **2**. These facts provide additional evidence (if such is needed) that the low-temperature process that leads to the exchange of alkoxyl groups in alkoxyphosphoranes is pseudorotation and not ring opening.

Acknowledgments. The authors wish to thank Professor E. J. Corey, who suggested the synthetic method used for the preparations of isopropylidene- and methyleneacetylacetone, Professor Donald Cram, who gave us permission to use his previously unpublished diagram for pseudorotation, and Dr. E. L. Muetterties, for helpful criticism of this manuscript. The authors also wish to acknowledge with gratitude Grant No. GP-6465X from the National Science Foundation that financed this investigation.

The Barriers to Pseudorotation in Cyclic Alkyloxyphosphoranes

David Gorenstein[1]

Contribution from the James Bryant Conant Laboratory, Harvard University, Cambridge, Massachusetts 02138. *Received May 15, 1969*

Abstract: In the previous paper, the syntheses and nmr spectra at various temperatures of a number of cyclic alkyloxyphosphoranes were presented. The exchange of groups on the phosphoranes at low temperatures, inferred from the spectra, was ascribed to pseudorotation about the phosphorus atom. The low-temperature exchange process overrides the barrier to placing an alkyl or aryl substituent in the apical position of the trigonal-bipyramidal molecule, whereas the exchange at high temperature, in specific cases, was shown to require either ring opening and reclosure or pseudorotation through an intermediate with a five-membered ring in diequatorial positions. In the present paper, the free energies and enthalpies of activation for the various exchange processes of phosphoranes have been determined. The line shapes expected for the nmr signals at various temperatures have been calculated and matched to the experimental spectra. In summary, the free energy of activation associated with placing an alkyl or aryl substituent in apical position varies, probably with steric effects, from 10 to 17 kcal/mol, whereas the free energy of activation both for ring opening and forming a diequatorial ring intermediate is around 20 kcal/mol.

In prior publications, the temperature dependence of the nmr spectra of alkylfluorophosphoranes[2] and of alkyl- and aryloxyphosphoranes[3–7] has been observed. The exchange of groups on the phosphorus atom has been inferred from these spectra, and the low temperature phenomena have been ascribed to "pseudorotation."[8] The rules under which pseudorotation can occur have been set forth, and in particular, we have shown[7] that the low-temperature process occurs by overriding the barrier[2] to placing an alkyl or aryl group in the apical position of a trigonal-bipyramidal intermediate. In the present paper, the free energies and enthalpies of activation for several low-temperature pseudorotation processes[7] have been determined by an analysis of the line shapes for the nmr signals obtained at various temperatures.

Furthermore, at higher temperatures, various phosphoranes related to acetylacetone undergo a ring-opening and reclosure process that leads to exchange of the methyl groups of the acetylacetone system, or, alternatively, they undergo a pseudorotation process that occurs by way of an unstable intermediate where a five-membered ring is placed in diequatorial positions.[7] The corresponding activation parameters have now been obtained from the temperature dependence of the nmr spectra associated with these phenomena.

Experimental and Computations

Methods. Nmr spectra were determined with a Varian A-60 or HA-100 spectrometer, equipped with a Varian V-6031 B variable-temperature probe. The usual precautions[9] were taken to ensure temperature stability, slow passage, avoidance of saturation, and maximum amplitude.

The computations for line shapes were carried out with an IBM 1620 digital computer, equipped with an auxillary storage disk and a Cal-Comp plotter. In general, computation of the line shape for each temperature for any one region in the spectrum of a compound required calculating 50 to 200 points, but took only from about 1 to 10 min of computing time on an IBM 1620. Thus even this slow computer proved adequate for the problem.

Uncoupled Two-Site Exchange. Many of the problems connected with this investigation involve simple uncoupled two-site exchanges. For example, the interchanges of the methyl groups in the acetylacetone moiety of various phosphoranes fall in this class. The calculation of the line shapes for these cases was made by the direct application of the familiar equation of Gutowsky, McCall, and Slichter.[10]

Coupled ABX Two-Site Exchange, $J_{AB} = 0$. The kinetic parameters for the interchange of the methoxyl groups in several phosphoranes, where the hydrogen atoms are coupled to phosphorus but not to each other, can be treated as two independent uncoupled two-site exchange processes. Analysis of the system shows that the intensity of absorption at any frequency can be calculated simply as the sum

---

[1] National Institutes of Health Predoctoral Fellow, 1967–1969. Address correspondence to author at: Chemistry Department, University of Illinois, Chicago Circle, Chicago, Ill.

[2] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), 20, 245 (1966); R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, 3, 753 (1964).

[3] D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **89**, 2762 (1967).

[4] D. Gorenstein and F. H. Westheimer, *Proc. Nat. Acad. Sci. U. S.*, **58**, 1747 (1967).

[5] F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968).

[6] F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.*, 90, 1275 (1968).

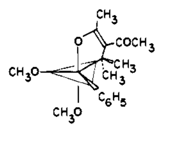
[7] D. Gorenstein and F. H. Westheimer, *ibid.*, 92, 634 (1970).

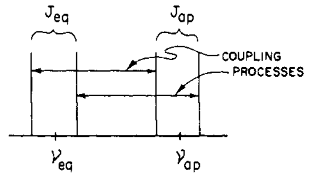
[8] R. S. Berry, *J. Chem. Phys.*, 32, 936 (1960).

[9] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinser, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).

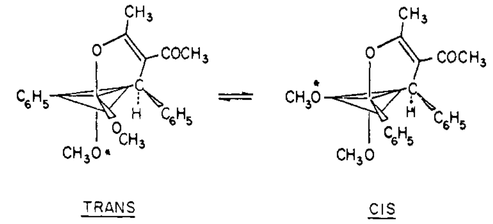
[10] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution NMR," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 218 ff.

of the intensities for two uncoupled two-site exchanges. For example, the spectrum obtained at low temperatures for the methoxyl groups of the adduct of dimethyl phenylphosphonite and isopropylidene acetylacetone consists of four lines, shown schematically below, and in detail in Figure 1. The signals can be ascribed to the equatorial and apical methoxyl groups; each signal is a doublet, with splitting by ^{31}P. The spectrum at higher temperatures can be calculated from that below 0° by applying the Gutowsky-McCall-Slichter equation to the two signals (one from each type of methoxyl group) that correspond to $M_I = -{}^1/_2$ for ^{31}P, then applying it again to the two signals that correspond to $M_I = +{}^1/_2$ for ^{31}P, and adding the computed intensities. This amounts to calculating the intensities from the Gutowsky-McCall-Slichter equation for exchange between groups with signals of the frequencies $\nu_{eq} - J_{eq}/2$ and $\nu_{ap} - J_{ap}/2$ and for exchange between groups with signals of the frequencies $\nu_{eq} + J_{eq}/2$ and $\nu_{ap} + J_{ap}/2$, where ν_{eq} and ν_{ap} are the frequencies corresponding to the centers of the equatorial and apical signals at low temperatures, and the *J*'s refer to the respective hydrogen-phosphorus coupling constants.

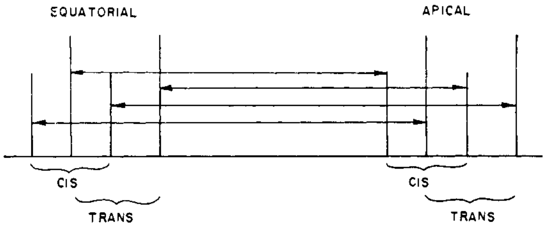




A more complicated situation arises for the addition product of dimethyl phenylphosphonite and benzylideneacetylacetone. Here, at low temperatures, the *cis* and *trans* isomers are individually identified, by their nmr spectra, in the approximate ratio of 1:2.



This spectrum at room temperature can be reproduced by assuming that an exchange process mixes the apical (starred) methoxyl group of the *trans* isomer with the equatorial (starred) methoxyl group of the *cis* isomer, and similarly this exchange process mixes the equatorial methoxyl group of the *trans* isomer with the apical methoxyl group of the *cis* isomer. These are the results predicted for pseudorotation processes.[3,7] The starred and unstarred methoxyl groups do not however exchange, since this would require an epimerization about the phosphorus atom[3,6,7] that cannot occur by pseudorotation under the restraint imposed by the strain rule. The line shapes for the exchange can be calculated by solving four simple two-site exchange problems, using the Gutowsky-McCall-Slichter equation and then summing the results. The pairs of frequencies from the low-temperature nmr spectrum needed for the calculation are indicated schematically below, where the arrows indicate the appropriate exchange processes.



Calculations were also performed for other assumed exchange processes, but they conspicuously failed to reproduce the observed spectra. One of these processes assumed interchange of one of the methoxyl groups of the *cis* isomer with the other methoxyl group of the same isomer (and similarly for the *trans*); the other process assumed interchange of the equatorial methoxyl group of the *cis* isomer with the equatorial methoxyl group of the *trans*, and similarly assumed exchange of the apical methoxyl groups. Of those alternatives considered, only the assumption of the pseudorotation mechanism produced calculated spectra that agree with those observed.

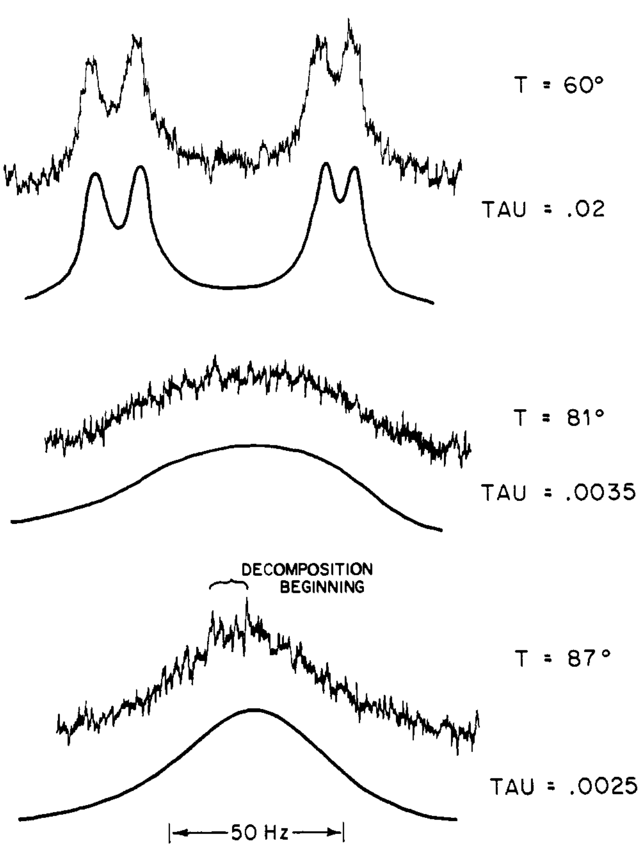


Figure 1. Calculated and observed nmr signals (100 Mc) from the methoxyl groups of the adduct of dimethyl phenylphosphonite and isopropylideneacetylacetone (bromobenzene as solvent).

Specifically, the equations used for calculating the intensity of absorption, *I*, as a function of the frequency, ω, for the coupled two-site exchange process are as follows

$$I(\omega) = \frac{-\kappa\{[1 + \tau/T_2]P + QR\}}{P^2 + R^2}$$

where

$$P = \tau\left[1/T_2{}^2 - (\Delta\omega)^2 + \left(\frac{\delta\omega}{2}\right)^2\right] + 1/T_2$$

$$Q = \tau\left[\Delta\omega - \left(\frac{\delta\omega}{2}\right)(p_A - p_B)\right]$$

$$R = \Delta\omega\left[1 + \frac{2\tau}{T_2}\right] + \frac{\delta}{2}\omega(p_A - p_B)$$

and

$$\Delta\omega = \frac{\omega_A + \omega_B}{2} - \omega;\ \delta\omega = \omega_A - \omega_B$$

$$\tau = \frac{\tau_A\tau_B}{\tau_A + \tau_B}$$

The proportionality constant, κ, was chosen arbitrarily to fit the intensity of the most intense peak. T_2 was set equal to 0.07 sec; its exact value does not affect the computation. p_A and p_B are the populations of the various states, and can be estimated from the nmr intensities. For a pseudorotation, $\tau_A = \tau_B = 1/k_{obsd}$ and $\omega = 2\pi\nu$, where ν is the frequency in cycles per second. For each value of τ, ω was varied from well below ω_A to well above ω_B.

Coupled ABCX Three-Site Exchange, $J_{AB} = J_{AC} = J_{BC} = 0$. The kinetic parameters for the interchange of the methoxyl groups for the adducts of trimethyl phosphite can be treated as independent uncoupled three-site exchange processes where the hydrogen atoms are coupled to phosphorus but not to each other. The intensity of the

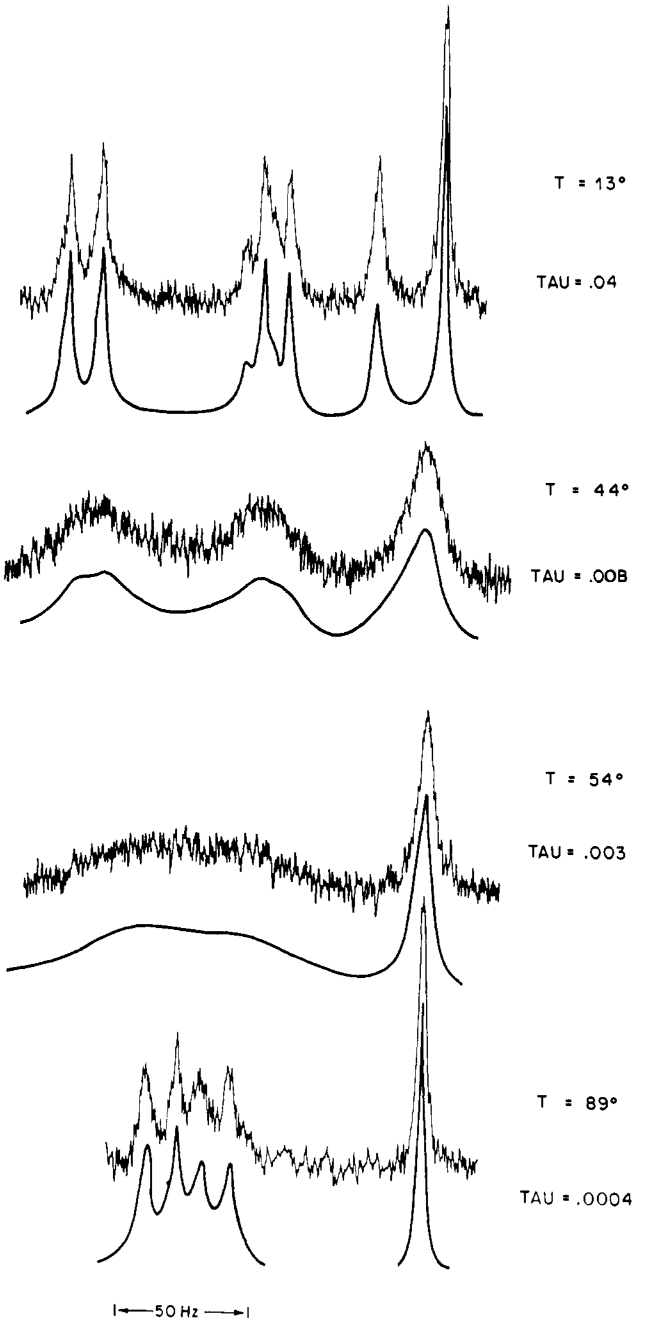


Figure 2. Calculated and observed nmr signals (60 Mc) for the methoxyl groups (low field) and vinyl methyl group (high field) of the *cis* and *trans* adducts of dimethyl phenylphosphonite and benzylideneacetylacetone (bromobenzene as solvent).

absorption at any frequency can be calculated as the sum of the corresponding intensities for the relevant absorptions, where M_I for phosphorus equals $\pm {}^1/_2$. The line-shape equation for the coupled three-site case was obtained by a simple extension of the Gutowsky–McCall–Slichter equation, following established methods.[10–12]

For the three-site ABCX exchange, where $J_{AB} = J_{AC} = J_{BC} = 0$

$$I(\omega) = \kappa\left[\frac{2D(A+B+C)R + (AB+BC+AC-3D^2)P}{P^2+R^2}\right]$$

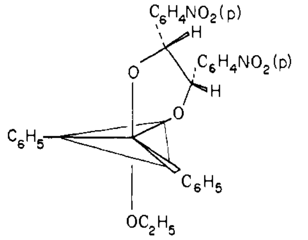
where

$$P = \left(\frac{1}{T_2} + \frac{2}{\tau}\right)(AB + BC + AC) - D^2/T_2$$

$$R = \left(\frac{1}{T_2} + \frac{1}{\tau}\right)(A + B + C)D - ABC$$

and $A = \Delta\omega_A$; $B = \Delta\omega_B$; $C = \Delta\omega_C$; $D = (1/T_2) + (3/\tau)$; $\tau = 1/k_{obsd}$. This equation must be applied to each pair of signals split by ^{31}P.

Coupled ABX Two-Site Exchange, $J_{AB} \neq 0$. In either stereoisomer of the condensation product of 1 mol of ethyl diphenylphosphinite with 2 mol of *p*-nitrobenzaldehyde,[7] the two methine hydrogen atoms are coupled both to each other and to phosphorus. (The isomer below, has been shown as *meso* for the sake of illustration, although the configuration of the compound in hand has not been established.) When pseudorotation occurs, the two methine hydrogen atoms undergo exchange. Since in this case $\omega_{AB} \sim J_{AB}$, the problem cannot be treated so simply as for the preceding cases; the appropriate equations were obtained through the density-matrix formulation as developed by Kaplan,[13] and elaborated by Alexander[14] and Johnson.[15]



For the two-site coupled ABX exchange

$$I(\omega) = \kappa\left[\frac{(A_+ + B_+ + J_{AB})(R_+) + 2\left(D - \frac{1}{\tau}\right)(P_+)}{P_+^2 + R_+^2} + \frac{(A_- + B_- - J_{AB})(R_-) + 2\left(D - \frac{1}{\tau}\right)(P_-)}{P_-^2 + R_-^2}\right]$$

where

$$P_\pm = D^2 - A_\pm B_\pm - \frac{1}{\tau^2} + J_{AB}^2/4$$

$$R_\pm = D(A_\pm + B_\pm) \pm J_{AB}/\tau$$

$$A_\pm = \Delta\omega_A \pm J_{AB}/2;\ B_\pm = \Delta\omega_B \pm J_{AB}/2$$

$$D = -\frac{1}{\tau} - \frac{1}{T_2};\ \tau = 1/k_{obsd}$$

Results

The nature of the results obtained can be seen from Figures 1–4, showing the calculated and observed nmr spectra for the adduct of dimethyl phenylphosphonite and isopropylideneacetylacetone (two-site exchange, with coupling to phosphorus), the calculated and observed spectra for the adduct of dimethyl phenylphosphonite and benzylideneacetylacetone (two-site exchange for each of two isomers, with coupling to phosphorus), the calculated and observed spectra for the adduct of trimethyl phosphite and benzylideneacetylacetone (three-site exchange, with coupling to phosphorus), and the calculated and observed spectra for the condensation prod-

---

(11) C. P. Slichter, "Principles of Magnetic Resonance," Harper & Row, Publishers, New York, N. Y., 1963, p 35.

(12) G. Binsch, "Topics in Stereochemistry," Vol. III, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., 1968, p 108.

(13) J. I. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958); **29**, 462 (1958).

(14) S. Alexander, *ibid.*, **37**, 967, 974 (1962); **40**, 2741 (1964).

(15) C. S. Johnson, *ibid.*, **41**, 3277 (1964).

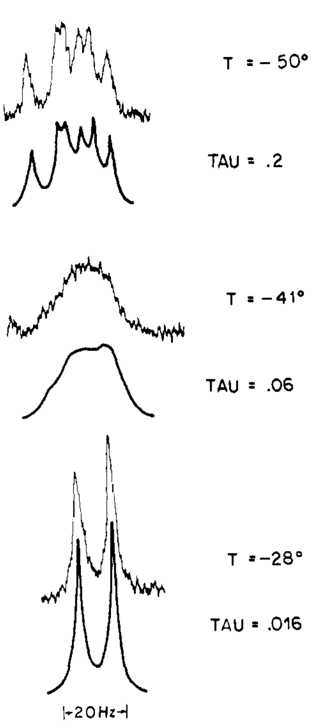


Figure 3. Calculated and observed nmr signals (60 Mc) for the methoxyl groups of the adduct of trimethyl phosphite and benzylideneacetylacetone (deuteriochloroform as solvent).

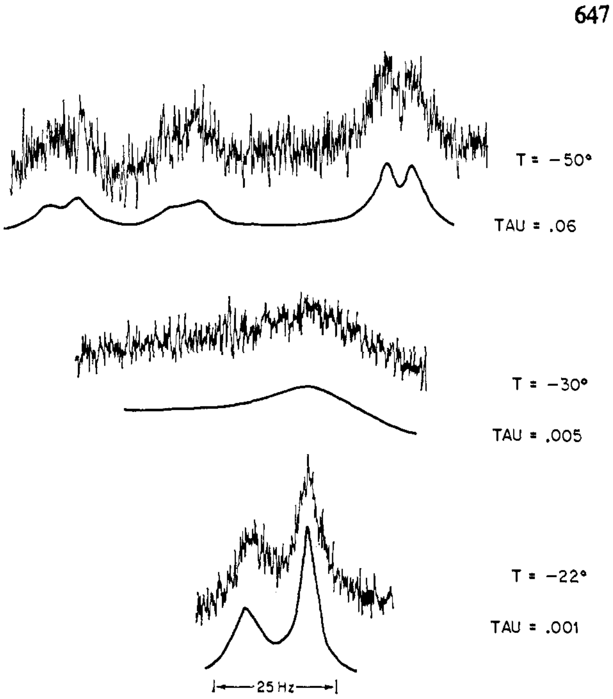


Figure 4. Calculated and observed nmr signals (100 Mc) from the methine hydrogen atoms of the adduct of ethyl diphenylphosphinite and 2 mol equiv of *p*-nitrobenzaldehyde (deuteriomethylene chloride as solvent).

uct of ethyl diphenylphosphinite with 2 mol of *p*-nitrobenzaldehyde (two-site exchange with the hydrogen atoms coupled to each other and to phosphorus). These figures provide examples of the agreement that was obtained with each of the four types of problem that was treated.

The line shapes calculated for various assumed time constants were fitted to the spectra obtained at various temperatures, so as to obtain a rate constant associated with each exchange process at a given temperature. The free energies of activation were obtained directly from the rate constants. The enthalpies of activation were obtained from the slopes of the plots of log (k_{obsd}/T) against $1/T$; a typical example is shown in Figure 5 for both pseudorotation and for ring opening in the adduct of dimethyl phenylphosphonite and isopropylideneacetylacetone. The entropies of activation follow from the corresponding free energies and enthalpies.

The data obtained in this way are presented in Table I.

Errors. When calculated spectra were compared to the observed spectra, good fits were obtained, but τ (and therefore k_{obsd}) could not generally be determined to better than ±20%, and the uncertainty in the temperature at which the best fit was obtained usually amounted to about 2° even near the coalescence temperature. When the chemical shift between the signals that coalesce is small (*e.g.*, 5 cps) the precision is of course less than when the chemical shift is larger (*e.g.*, 20 cps or more). These considerations led to estimates of error of 0.2–0.5 kcal/mol in $\Delta F^{\ddagger}$ for pseudorotation and for ring opening.

Application of least-squares techniques to the plots of $\log(k_{obsd}/T)$ against $1/T$ (to obtain $\Delta H^{\ddagger}$) led to the computation of probable errors of the order of 0.5 kcal/mol.

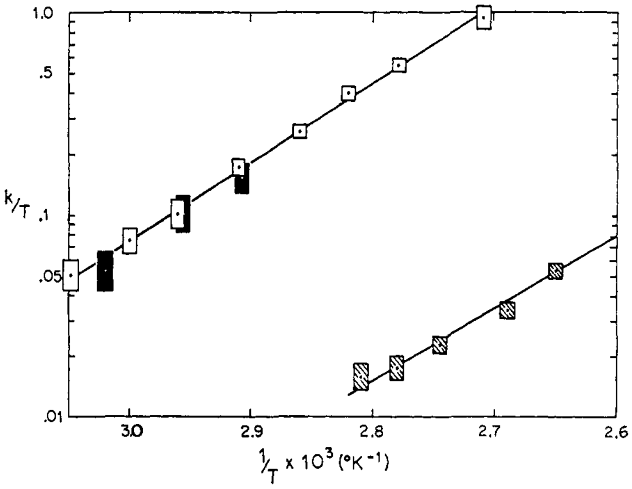
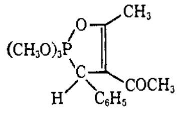
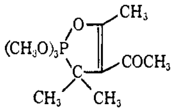
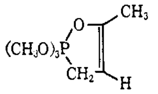
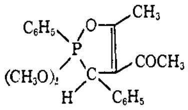
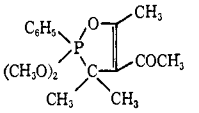
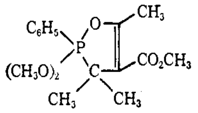
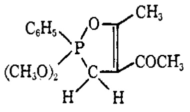
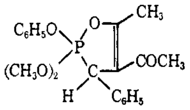
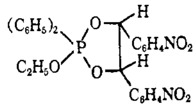


Figure 5. Determination of $\Delta H^{\ddagger}$ for the pseudorotation (upper line) and ring opening (lower line) for the adduct of dimethyl phenylphosphonite and isopropylideneacetylacetone. For the upper line, the open rectangles present data for the exchange process for methoxyl groups, whereas the solid rectangles present data for the exchange process for the methyl groups of the isopropylidene residue. The size of the rectangles gives a rough idea of the limits of error.

These computations are, however, misleading, and the limits of error so found are patently too narrow. Since the rate constants are uncertain to ±20% and since the temperature is uncertain in each measurement to ±2°, we estimate that, generally, the enthalpies of activation are uncertain to about 25%. These more generous error limits have been entered into Table I.

The entropies of activation are generally small (−15 to +10 eu) with uncertainties so large that the value of $\Delta S^{\ddagger}$ is never clearly distinguished from zero. As a first approximation, therefore, all of the entropies of ac-

Table I. Activation Parameters for Pseudorotation, Ring Opening, and Dissociation

Adduct	Pseudorotation[a]			Ring opening[a]			Dissociation
	$\Delta H^{\ddagger}$, kcal/mol	$\Delta F^{\ddagger}$, kcal/mol	T_c, °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta F^{\ddagger}$, kcal/mol	T_c, °C	$\Delta F^{\ddagger}$, kcal/mol
	$11.5 \pm 3^{c,i}$ $12.2 \pm 3^{d,h}$ $10.7 \pm 3^{c,h}$	11.8 ± 0.5 12.2 ± 0.5 11.8 ± 0.5	−40 −41 −37	$15.6 \pm 3^{e,i}$	21.2 ± 0.5	155	31 ± 0.5^{b}
	$11.6 \pm 4^{e,i}$ $8.8 \pm 4^{e,i}$	14.5 ± 0.5 14.5 ± 0.5	−5 −5	$13.3 \pm 3^{e,i}$	19.2 ± 1.0	84	29 ± 0.5^{b}
	$10.6 \pm 3^{g,h}$ $11.1 \pm 3^{g,i}$	9.7 ± 0.5 9.6 ± 0.2	−85 −84				
	$15.0 \pm 2^{e,i}$ $11.6 \pm 2^{e,i}$	15.8 ± 0.2^{j} 15.8 ± 0.2 $(>24)^{m}$	54 50 (>190)	$17.8 \pm 2^{e,i}$ $16.0 \pm 2^{e,h}$	20.3 ± 0.2 20.5 ± 0.2	131 126	$>29^{b}$
	$18.1 \pm 3^{e,i}$ $13.9 \pm 3^{e,h}$ $13.2 \pm 3^{e,i}$	17.4 ± 0.2 17.0 ± 0.2 17.0 ± 0.2	81 62 80	$16.8 \pm 3^{e,i}$ $15.8 \pm 3^{e,h}$	20.0 ± 0.2 20.3 ± 0.5 $19.8 \pm 1.0^{e,h}$	104 105 100	28.0 ± 0.5^{b}
	$12.6 \pm 3^{e,i}$ $12.9 \pm 3^{e,i}$	17.1 ± 0.5 17.1 ± 0.5	75 62				
	$6.8 \pm 3^{g,i}$ $6.8 \pm 3^{g,i}$	9.9 ± 1 9.5 ± 1	−63 −70				
	$14.9 \pm 3^{g,i}$ $10.4 \pm 4^{f,i}$ $(17.8 \pm 4)^{e,i}$	13.0 ± 0.5^{n} 12.0 ± 1^{n} (21.8 ± 0.2)	-4^{l} −26 (141)		$21.9 \pm 1.0^{e,i}$	>160	30 ± 0.5^{b}
	$13.8 \pm 3^{d,i}$	11.6 ± 1	−39				

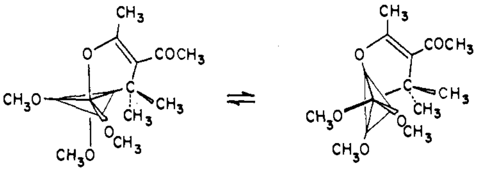
[a] Calculated from complete line-shape analysis. The limits of error for $\Delta H^{\ddagger}$ were obtained from the graphs of log k_{obsd}/T against $1/T$. The coalescence temperatures, T_c, refer to the temperatures of maximum broadening of the nmr signals from the methoxyl groups (pseudorotation) or from the methyl groups (ring opening and reclosure). [b] In bromobenzene at 110°. [c] In acetone-d_6. [d] In chloroform-d_1. [e] In bromobenzene. [f] In toluene-d_8. [g] In methylene chloride-d_2. [h] At 60 Mc. [i] At 100 Mc. [j] *cis* isomer. The free energy for equilibration, $F_{trans}° - F_{cis}° = 0.3 \pm 0.1$ kcal/mol. [k] Calculated for epimerization at phosphorus from the signals of the methoxyl groups. [l] Coalescence temperature for the equilibration of the two observable isomers of the phosphorane as measured by the collapse of the two signals observed for the acetyl methyl group and for the concomitant collapse of the two signals for the vinyl methyl group. [m] Calculated for epimerization at phosphorus. The lower limit was obtained by noting that the methoxyl groups do not collapse even at a temperature of 190°. [n] Mean activation parameters. The free energy for equilibration, between the two observed isomers, $F_1° - F_2° \simeq 0.7$ kcal/mol.

tivation are considered as zero, and the individual values have not been entered into Table I.

Discussion

In the accompanying paper,[7] a consideration of the possible pathways for interchange of groups in a phosphorane confirmed the conclusion[3-6] that the low-temperature process, observed by nmr spectroscopy, is pseudorotation. Such a pseudorotation process occurs when the energy is sufficient to allow the formation of an intermediate where an alkyl or aryl group occupies an apical position of a trigonal-bipyramidal molecule. Muetterties' preference rule[2] states that such structures are less stable than those where the alkyl and aryl groups are equatorial. Table I shows that the free energy of activation for surmounting this barrier, *in the compounds here examined*, falls in the range from 10 to 17 kcal/mol. The enthalpies of activation are similar.

A convenient way to visualize the pseudorotation barriers is shown in Figure 6. In the accompanying paper, the possible pathways were shown for the conversion of each isomer to others by pseudorotation. In a phosphorane molecule that contains a five-membered ring, the strain rule is obeyed; *i.e.*, at low temperatures only those isomers are formed where the ring occupies one equatorial and one apical position. Under these circumstances, the pathway for pseudorotation is circular, leading after six pseudorotations back to the starting material.[7] The pseudorotation processes for phosphoranes with five-membered rings do not, however, admit the possibility of epimerization (or, where appropriate, racemization) about the central phosphorus atom. The circular pathway of Figure 6 represents the allowed pseudorotations of the adduct of trimethyl phosphite and isopropylideneacetylacetone. Each minimum corresponds to a structure with the oxygen atom of the ring in one apical position as shown, but with a different methoxyl group in the other apical position; each maximum refers to an intermediate where the *gem*-dimethyl group occupies one apical position, but where a methoxyl group (a different one in each pseudorotamer) occupies the other apical position. The question has not yet been decided as to whether these high energy structures represent transition states (as shown in Figure 6) or whether they represent intermediates. If the latter proves correct, then Figure 6 should be modified to show shallow minima where the three maxima are drawn, with transition states close by on either side of these shallow minima.



STRUCTURE AT MINIMA

STRUCTURE AT MAXIMA

Steric Effects. The best explanation so far available for the differences in free energy of activation for pseudorotation at low temperatures among the various phosphoranes here shown is steric. There is little difference in free energy of activation for pseudorotation between the adduct of methyl vinyl ketone with trimethyl phosphite, and the corresponding adduct of dimethyl phenylphosphonite and methyleneacetylacetone. These two compounds are similar in that a simple methylene group, with minimum steric requirements, is attached to the central phosphorus atom. On the other hand, the two compounds are quite different with respect to electronic effects; the carbonyl group in the adduct of methyleneacetylacetone must cause considerable polarization.[16]

By contrast, the condensation products with a benzyl group or a *gem*-dimethyl group on the tetrahedral carbon atom of the ring show moderately high free energies of activation for pseudorotation. These facts suggest that the energy of an unstable intermediate (corresponding to a maximum in a diagram similar to that shown in Figure 6) is increased by bulky groups in the apical position.

The steric effects here suggested are not however easy to visualize in terms of space-filling models; the various groups do not appear to interfere with one another. Perhaps the effect will prove to be steric hindrance to solvation. An alternative but less attractive hypothesis attributes at least part of the effect to differences in group electronegativities. However, whatever the reason for the higher energies associated with the *gem*-dimethyl and benzyl groups, the temperature-dependent nmr spectra show that they are real.

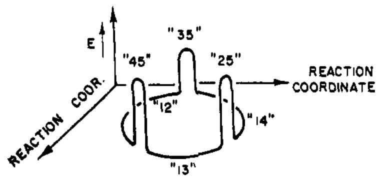


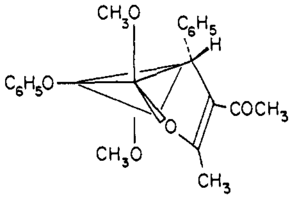
Figure 6. Schematic energy diagram for a series of pseudorotations for a symmetrical adduct (*e.g.*, that of trimethyl phosphite and isopropylideneacetylacetone). See ref 7 for numbering of isomers.

If the explanation in steric terms proves correct, it might bear upon the question of the activation energy for the hydrolysis of methyl ethylene phosphate. The heat of hydrolysis of methyl ethylene phosphate exceeds that for an acyclic analog by about 5.5 kcal/mol,[17] whereas the activation energy for its hydrolysis is less than that for trimethyl phosphate by 7.5 kcal/mol.[18] Possibly the difference between these figures is related to greater steric interference in the trigonal-bipyramidal transition state for the hydrolysis of trimethyl phosphate than in that for the hydrolysis of methyl ethylene phosphate.

High-Temperature Processes. Three separate high-temperature processes have been identified in alkyloxyphosphoranes.

(1) The spectra of alkyloxyphosphoranes related to acetylacetone may be interpreted to show exchange between the two methyl groups of the acetylacetone system, without accompanying exchange of the methoxyl residues. This exchange process has previously been identified as one that occurs by way of ring opening and reclosure, through an open-chain zwitterionic intermediate.[4,6,7] The free energy of activation for this process, in all of the compounds so far examined, has here been found (see Table I) to be about 20 kcal/mol. This process then (at least for derivatives of acetylacetone) requires considerably more activation than does pseudorotation.

(2) The unique high-temperature nmr spectra of the adduct of dimethyl phenyl phosphite and benzylideneacetylacetone were presented in the previous paper.[7] Above 140°, the nmr signals for the two methoxyl groups simplify to a doublet, indicating that at this temperature these groups are rapidly interchanging positions. This interchange has been explained as occurring by way of an intermediate where the five-membered ring occupies two equatorial positions on the phosphorane structure.[7] One of the possible structures, with the ring in diequatorial positions, is shown below. Since, at high temperatures, the phosphorane



---

[16] Equilibration of the methoxyl groups in the adduct of dimethyl phenylphosphonite requires, in successive pseudorotamers, that the phenyl group and the methylene group be placed in apical positions. Thus the activation energy for the exchange process will reflect the energy of the less stable of these intermediates. By contrast, equilibration of the methoxyl groups in the adduct of trimethyl phosphite and methyl vinyl ketone requires only that one unstable intermediate—one with an apical methylene group—be formed. Since the activation energies for the equilibration processes for the two compounds are similar, the pseudorotamer with apical phenyl group cannot be especially unstable.

[17] E. T. Kaiser, M. Panar, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **85**, 602 (1963).

[18] F. Covitz, Thesis, Harvard University, 1965.

also undergoes ring opening and reclosure, the actual structure may be distorted, with an elongated bond or considerable deviation from the geometry of a regular trigonal bipyramid. Therefore the excess energy of a compound with a five-membered ring in the idealized geometry shown below might be even greater than the activation energy for pseudorotation here observed.

We conclude then that the activation energy of 22 kcal/mol, determined from the nmr spectra of the adduct of dimethyl phenyl phosphite and benzylidene acetylacetone, is associated with surmounting the barrier imposed by the strain rule. This energy is considerably greater than that required to place an alkyl or aryl group in apical position, *i.e.*, to surmount the barrier imposed by Muetterties' rule.[19] The activation energy for the opening of the ring in the adduct of phenyl dimethyl phosphite and benzylideneacetylacetone is also about 22 kcal/mol. But the two processes—ring opening and pseudorotation through an intermediate with the ring in diequatorial positions—have quite different consequences for the nmr spectra and are thus distinct. The former results in mixing the signals from the methyl groups of the acetylacetone system, without mixing those of the methoxyl groups whereas the latter mixes the signals of the methoxyl groups without mixing those from the methyl groups.

(3) Finally, it must be noted that at high temperatures the phosphoranes under discussion partially dissociate to the compounds from which they were formed, *i.e.*, to an alkylideneacetylacetone and a phosphite or phosphonite. This process, however, is slow compared to those previously discussed. The rates can be measured by conventional, rather than nmr techniques and are accompanied by activation free energies in the range of 30 kcal/mol.

Acknowledgments. The author wishes to thank Professor F. H. Westheimer, who suggested this problem, for his help and encouragement. He also wishes to acknowledge with gratitude the Grant GP-6465X from the National Science Foundation that made this work possible.

(19) Muetterties, Mahler, and Schmutzler[20] have offered evidence that the ring in tetramethylene trifluorophosphorane occupies diequatorial positions. In this compound, the barrier imposed by Muetterties' rule apparently exceeds that imposed by the strain rule. Since fluorine is so much more electronegative than oxygen, the contrast between the behavior of the oxyphosphoranes and that of the fluorophosphoranes appears reasonable.

(20) E. L. Muetterites, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963).

On the Mechanism of Sulfonamide Cleavage by Arene Anion Radicals[1a]

W. D. Closson,[1b] Sungchul Ji, and Shirley Schulenberg

Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12203. *Received July 12, 1969*

Abstract: In the cleavage of sulfonamides of secondary amines with arene anion radicals 2 moles of the reducing species are consumed rapidly, resulting in formation of amide and sulfinate anions. In the case of arenesulfinate ion a subsequent, much slower reduction converts this to arene hydrocarbon and a mixture of thiosulfate, sulfite, and sulfide salts. By analysis of competitive reactions, the rate law for the first step has been deduced as rate = *k*[anion radical][sulfonamide]. In the reaction of sodium naphthalenide (and probably sodium biphenylide) with the toluenesulfonamide of *p*-toluidine, electron transfer and cleavage are considerably faster than acid–base reaction with the acidic proton. Sodium anthracenide, however, reacts only as a base with this substrate. Gross structural effects on the scope of the reaction are discussed.

The discovery of the efficient cleavage of arenesulfonamides[2] and toluenesulfonate esters[3] with the anion radicals derived from aromatic hydrocarbons by treatment with alkali metals in ether solvents has prompted us to examine the mechanisms of these potentially useful reactions. Some results and conclusions concerning the anion radical cleavage of sulfonamides are presented in this paper.

Preliminary examination of the reaction of several sulfonamides with sodium naphthalenide at room temperature in 1,2-dimethoxyethane (DME) indicated a rather variable stoichiometry. One equivalent of sulfonamide would require from 2 to almost 6 equiv of anion radical for complete cleavage to the anion of the corresponding amine. It was found, however, that at low temperatures (−60 to −80°) complete cleavage of arenesulfonamides of secondary amines required exactly 2 equiv of sodium naphthalenide. The rate of reaction of a typical arenesulfonamide is still quite rapid at these temperatures, and with suitable apparatus it is possible to titrate the sulfonamide solution, reaching a faint green end point when all of the sulfonamide is consumed. In fact, this represents an excellent method for standardization of sodium naphthalenide or biphenylide solutions in DME. (Unfortunately, the same reactions in tetrahydrofuran (THF) solution usually develop a brown color that seriously interferes with determination of the end point.) In Figure 1 is shown a typical titration plot for reaction of N-methyl-N-phenyl-*p*-toluenesulfonamide (I) with sodium naph-

(1) (a) Supported in part by the Public Health Service (Research Grant No. R01-AM11419 from the National Institutes of Arthritis and Metabolic Diseases). (b) Alfred P. Sloan Research Fellow, 1968–1970.

(2) S. Ji, L. B. Gortler, A. Waring, A. Battisti, S. Bank, W. D. Closson, and P. Wriede, *J. Am. Chem. Soc.*, 89, 5311 (1967).

(3) W. D. Closson, P. Wriede, and S. Bank, *ibid.*, 88, 1581 (1966).