vessel consisted of two bulbs sealed to one another and to a third smaller piece of tubing having a male joint appropriate for attachment to a vacuum line. Two or three olefinic or benzylic substrates, plus the initiator or inhibitor, were accurately weighed directly into one of the bulbs of the reaction vessel. The N-bromoimide was weighed into the other bulb and 5 ml of benzene added to each bulb. The reaction mixture was degassed three times at 0.05–0.1 mm, sealed, immersed in an oil bath at 80°, allowed to reach thermal equilibrium (3-4 min), and the contents of the bulbs were rapidly mixed. Upon mixing, the solution of the N-bromoimide was always added, with swirling, to that of the substrates.

Competitive NBS brominations at 25° were carried out in purified benzene using benzoyl peroxide as initiator. The reaction vessel used was a cylinder 1 ft long and 3 in. in diameter, sealed at one end with a vacuum stopcock and male joint at the other. All components of the reaction mixture were weighed, dissolved in benzene, and transferred quantitatively to the reaction vessel. The reaction medium was degassed three times, sealed from the atmosphere by a stopcock, immersed in a water bath at 25°, and irradiated with magnetic stirring for 4 hr, using a 270-W G.E. sunlamp.

Glassware used in the competitive rate studies was treated with aqua regia for 1 hr at 100°, rinsed with water, treated with concentrated ammonium hydroxide, rinsed repeatedly with water, and dried at 150–200°.

Bromination by Molecular Bromine. Brominations employing molecular bromine were carried out at 25 ± 2° in benzene. The reaction vessel was a 1000-ml round-bottomed flask modified such that the tips of four capillary tubes could be immersed into the reaction mixture nearly to the base of the flask. The weighed reaction substrates were dissolved in 250 ml of benzene in the reaction vessel and immersed in a water bath at 40° with magnetic stirring. A steadily increasing flow of nitrogen (Matheson prepurified) was introduced into the solution *via* three capillary tubes. Such a procedure served both to slowly lower the temperature and to deoxygenate the reaction medium. A G.E. sunlamp was used to irradiate the solution. When the desired temperature (25°) was attained, the nitrogen flow was rerouted through a by-pass allowing a weighed quantity of dilute gaseous bromine to be carried into the reaction medium. After an induction period of a few seconds (usually 2-5 sec), the light red-brown color of bromine in the solution was no longer noticed and the presence of hydrogen bromide in the exit gases was immediately evident. Since the reaction time (60–90 sec) was so short more extensive efforts at temperature control were considered unnecessary. A 270-W G.E. sunlamp provided the ultraviolet radiation.

Analysis of the Product Mixtures. The addition of weighed quantities of an internal standard (phthalide) to the product mixture allowed ready analysis of the reaction products by nmr spectroscopy. In general, five integrals were run for every sample and deviations seldom exceeded ±2%. Concentration of the product mixtures, where necessary, was carried out using a rotary evaporator at 40° (80–120 mm).

The Quantitative Determination of 1,1-Bis(*p*-*t*-butylphenyl)-2,2-dimethyl-d_6-ethylene (11) in Product Mixtures. In runs where the deuterated olefin **1i** was used as a competitive substrate, mass spectrometry was used to determine the final quantity of this substrate present in the reaction medium after reaction. The undeuterated analog **1b** was weighed into the reaction mixture immediately after the reaction was complete to serve as an internal standard. Comparison of the heights of the peaks at *m/e* 320 and 326 allowed accurate calculation of the quantity of **1l** remaining after reaction. In those runs where the standard served also as a competitive reactant, nmr analysis was employed in determining the quantity of this olefin remaining after reaction.

Work-up consisted of careful removal of solvent, passage of the nonvolatile remaining oil in pentane through Florisil and/or alumina to remove the product bromides, and mass spectrometric analysis of the recovered mixture of olefins. Control analyses of mixtures of known quantities of **1l** and **1b** gave agreement between measured and known ratios within ±2%.

Acknowledgment. This work was supported in part by a grant from the U. S. Public Health Service, GM-12296.

Nuclear Magnetic Resonance Evidence for the Pathways of Pseudorotation in Alkyloxyphosphoranes

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

Abstract: In previous communications[2,3] we showed that alkyloxyphosphoranes containing five-membered rings undergo pseudorotation about the pentacovalent phosphorus atom, subject to the constraints imposed by considerations of ring strain and of the preference for placing alkyl groups in equatorial positions. A process of ring opening and reclosure, which can equilibrate some of the groups in a phosphorane, was also found, but only at high temperatures, and is clearly distinguished from pseudorotation. A number of new alkyloxyphosphoranes have now been synthesized; a study of their nmr spectra shows that, at least in most instances, pseudorotation occurs by surmounting the energy barrier required to place an alkyl group in an apical position. In addition, a second and different process occurs in one phosphorane to equilibrate groups that are not mixed by the usual pathway for pseudorotation. Possibly the substantially higher barrier that is associated with this second process is that required to place a five-membered ring in diequatorial positions in a phosphorane. Additional experiments confirm and make more secure the distinction between ring opening and pseudorotation in cyclic alkyloxyphosphoranes.

The chemistry of cyclic esters of phosphoric acid and of related esters of phosphonic and phosphinic acids has led to the concept[4–9] that the hydrolysis of these esters may, and on occasion must be accompanied

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

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

[4] E. A. Dennis and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3431 (1966); *ibid.*, **88**, 3432 (1966).

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

[6] R. Kluger and F. H. Westheimer, *J. Amer. Chem. Soc.*, **91**, 4143 (1969).

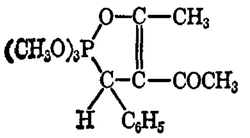
[7] R. Kluger, F. Covitz, E. A. Dennis, L. D. Williams, and F. H. Westheimer, *ibid.*, **91**, 6066 (1969).

[8] D. S. Frank and D. A. Usher, *ibid.*, **89**, 6360 (1967).

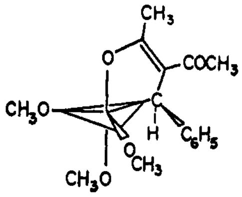
[9] W. Hawes and S. Trippett, *Chem. Commun.*, 577 (1968).

by pseudorotation[10] about the central phosphorus atom. The study of the nmr spectra of oxyphosphoranes, as the earlier studies of fluorophosphoranes,[11] has demonstrated that the process occurs readily, and has illuminated the constraints on the process and the preference rules for the formation of trigonal-bipyramidal compounds of pentacovalent phosphorus.

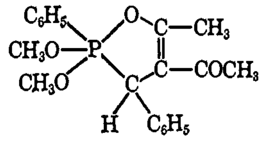
Earlier Findings. The pertinent nmr findings and the problems that remained can be summarized as follows: in a previous communication,[2] we showed that the nmr spectrum of **1a** is temperature dependent. At low temperatures, the molecule is frozen on the nmr time scale in the conformation **1b**, as evidenced by the finding that, in deuteriochloroform as solvent, the three methoxyl groups give individual nmr signals; by contrast, at room temperature the three methoxyl groups give the same signal.[12] (Each of the proton signals referred to above is a doublet, with splitting by ^{31}P.) We postulated[2] that at room temperature the methoxyl groups become equivalent on the nmr time scale by pseudorotation. This idea was strongly supported by a detailed analysis[3,5,13] of the nmr spectrum of compound **2**. At low temperature **2** consists of a mixture of the *trans* and *cis* isomers, **2b** and **2c**. At 50° the isomers are equilibrated by pseudorotation in accordance with the restraints imposed by a polarity rule[11] and a strain rule.[5,14] However, (as explained in detail in the Discussion) the methoxyl groups of **2** do not become completely equivalent, even at high temperatures and in particular the starred groups do not exchange with the unstarred ones.[15]



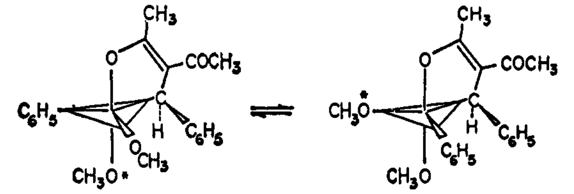
1a



1b

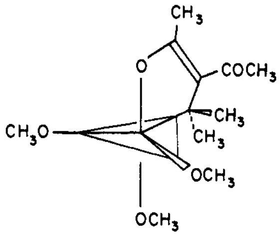


2a



2b **2c**

New Tests of Theory. Some of the distinctive features of the nmr spectrum of the isomers of **2** depend upon the presence of an asymmetric carbon atom in the five-membered ring. In order to test the validity of the assignments previously offered, we have now prepared a number of compounds where the tetrahedral carbon atom of the ring is symmetrically substituted. These compounds include **3**, **4**, **5**, **6**, and **7**, where, in each formula, a phosphorus atom is assumed at the center of the trigonal-bipyramidal system.



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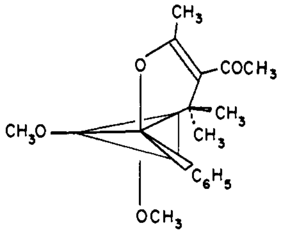

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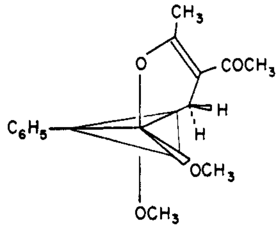

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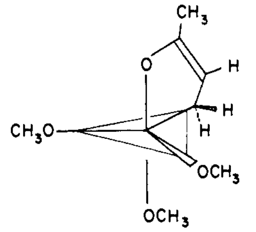

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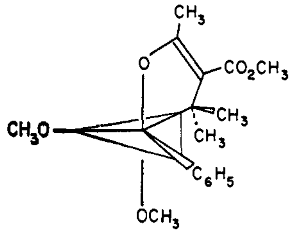

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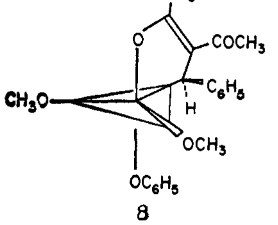
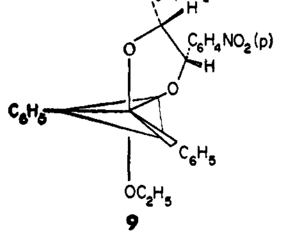
Two further compounds, **8** and **9**, were also prepared to extend our understanding of the pseudorotation pro-



8



9

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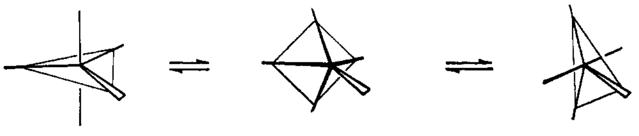
(10) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960). "Pseudorotation" is used here and in the following paper to mean an intramolecular process in trigonal-bipyramidal molecules which requires relatively small motion of the atoms, with accompanying deformation of the bond angles, as shown in the diagram below.



The internal motion is such that the original trigonal bipyramid appears to have been rotated by 90° about an axis between the phosphorus atom and the equatorial substituent (the "pivot") nearest the reader.

(11) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), 20, 245 (1966); E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963); E. L. Muetterties, W. Mahler, K. J. Parker, and R. Schmutzler, *ibid.*, 3, 1298 (1964); R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, 4, 496 (1965); R. Schmutzler and F. S. Reddy, *Inorg. Chem.*, 4, 191 (1965).

(12) F. Ramirez, O. P. Madan, and S. R. Heller, *J. Amer. Chem. Soc.*, 87, 731 (1965).

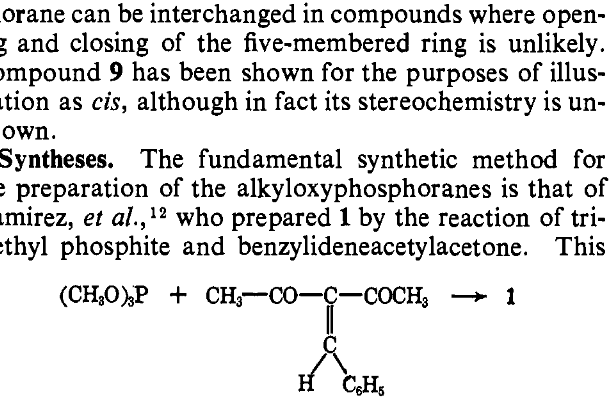
(13) F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *ibid.*, 90, 1275 (1968); 90, 3299 (1968).

(14) P. C. Haake and F. H. Westheimer, *ibid.*, 83, 1102 (1961); D. A. Usher, E. A. Dennis, and F. H. Westheimer, *ibid.*, 87, 2320 (1965).

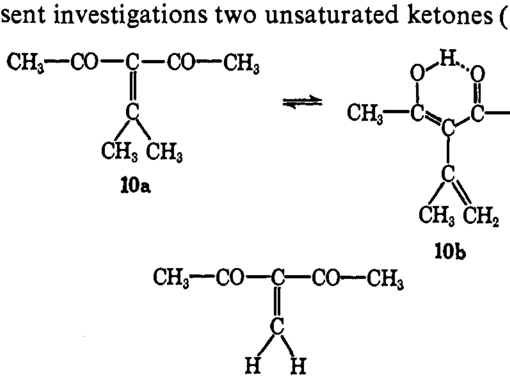
(15) The fact that the two classes of methoxyl groups do not become equivalent is established by their nmr spectra. In our prior publication, we reported that at 60 MC the signals from the methoxyl groups appear as a triplet, which we interpreted as two overlapping doublets.[3] We have now confirmed this interpretation; at 100 Mc, the high-temperature spectrum of 2 shows two doublets, separated by a chemical shift of 20.0 cps with J_{H-P} of 11.3 and 11.6 cps.

cess. Compound **8** was synthesized because, although it has the same symmetry as **2**, it has only one, rather than two phosphorus–carbon bonds. Compounds **6** and **9** can be used to test whether the groups of a phosphorane can be interchanged in compounds where opening and closing of the five-membered ring is unlikely. Compound **9** has been shown for the purposes of illustration as *cis*, although in fact its stereochemistry is unknown.

Syntheses. The fundamental synthetic method for the preparation of the alkyloxyphosphoranes is that of Ramirez, *et al.*,[12] who prepared **1** by the reaction of trimethyl phosphite and benzylideneacetylacetone. This



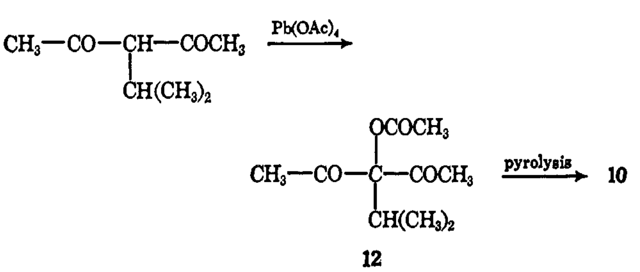
synthesis has been modified in the past to prepare other alkyloxyphosphoranes.[3,13,16] For the purposes of the present investigations two unsaturated ketones (**10a** and


10a

10b

11

11) were required. Although the esters of isopropylidene acetoacetate had been prepared[17] (and the methyl ester reacts normally with phosphonites; see Experimental Section), isopropylideneacetylacetone was unknown. It was here prepared by a synthesis suggested by Professor E. J. Corey.


12

The material exists as a keto–enol mixture. Either isomer can be isolated by careful distillation; the enol can be obtained nearly pure from the lower boiling fractions, and the ketone nearly pure from the pot residue.[18] Enolization from the γ position of α,β-unsaturated carbonyl compounds is a well-known process[19] and enols analogous to those shown here have been obtained for butylidene- and isovalerideneacetylacetone[20] and for 2-acetylcyclohex-2-en-1-one.[21] In the present example, in contrast with earlier ones, both isomers were obtained from the equilibrium mixture. Although reaction between a phosphite or phosphonite and an α,β-unsaturated ketone presumably occurs only with the keto tautomer, synthesis of phosphoranes proceeds in satisfactory yields from the keto–enol mixture of **10**, where the rate-limiting step for the reaction with the enol is presumably tautomerization.

The synthesis of **11** was carried out in a manner analoguous to that of **10**. As might have been anticipated, methylene acetylacetone is highly reactive and polymerizes readily. Although we were unable to keep it long enough for analysis, the crude material shows the correct exact mass, and reacts readily with dimethyl phenylphosphonite to yield a stable phosphorane.

Experimental Section

Materials. 3-Isopropylideneacetylacetone (**10**) was prepared by a modification of the methods of Dimroth and of DePuy.[22] A mixture of 42 g of isopropylacetylacetone[23] and 150 g of lead tetraacetate in 40 ml of benzene was heated at 75° for 10 hr under nitrogen. The crude product, analyzed by vpc on a $^1/_4$ in. × 6 ft column of SF-96-Chromosorb W at 160° with 60 cc/min flow of helium, consisted of 40% starting material, 38% product (2-acetoxy-2-isopropylacetylacetone), and 18% of an impurity tentatively identified by its nmr spectrum as O-isopropyl acetylacetone. Addition of 40 g more of lead tetraacetate and a further 20 hr heating at 75° increased the yield of product to 60%. The suspension of products was washed with water several times, the aqueous layer backwashed with benzene, and the benzene layer finally washed with a little water to help remove acetic acid. The benzene was removed on a Büchi evaporator, and the 70 g of residue distilled through a 1-ft jacketed Vigreux column. The product, **12** (18.5 g), was distilled at 134–140° (34 mm), and was identified by nmr spectroscopy and analysis.

3-Isopropyl-3-acetoxyacetylacetone (10 g) was passed at a rate of 5–10 drops/min through a 1 × 20 cm tube packed with 0.5-cm glass helices and heated to 550–590°; the compound was carried by a stream of 50 cc/min of nitrogen. The crude product (analyzed by vpc) consisted of 60% of the keto–enol mixture of isopropylideneacetylacetone, together with acetic acid, starting material, and 12% of an unknown impurity. Fractional distillation yielded 3.1 g of a 40:60 keto–enol mixture of isopropylideneacetylacetone boiling from 85 to 100° at 30 mm. Redistillation gave pure **10b**, bp 94° (41 mm). The distillate is nearly pure enol as seen from its nmr spectrum in carbon tetrachloride. The vinyl methyl protons appear as a doublet of doublets at δ 1.92 (3 H) with J_{trans} = 1.6 cps and J_{cis} = 0.9 cps. A singlet at δ 2.05 (6 H) is attributed to the two methyl groups of the acetylacetone system and the two multiplets at δ 4.9 (1 H) and 5.25 (1 H) with J_{gem} = 2.4 cps are attributed to the two vinyl protons. Finally, the enolic proton appears as a singlet at δ 16.1 (1 H). The last trace of pot residue is nearly pure ketone, again identified by its nmr spectrum in carbon tetrachloride. The isopropylidene protons appear as a singlet at δ 1.92 (6 H) and the protons from the two methyl groups of the acetylacetone system appear as a singlet at δ 2.22 (6 H). The ultraviolet spectra of the two tautomers show that the keto tautomer absorbs at 228 mμ with an ϵ of 10,500, whereas the enol absorbs at 287 mμ with an ϵ of 8600. The equilibrium mixture, analyzed by uv or nmr, contains 40% ketone and 60% enol.

3-Methyleneacetylacetone, 11. Freshly distilled (enolic) 3-methylacetylacetone[24] was similarly oxidized with lead tetraacetate (12 hr at 30°) and the 3-acetoxy-3-methylacetylacetone (bp 103° (16 mm)) **13**, was identified by nmr spectroscopy and analysis. It was pyrolyzed at 550–590°, and the resulting crude product, **11**, was

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[16] F. Ramirez, *Bull. Soc. Chim. Fr.*, 2443 (1966).

[17] H. Pauly, *Ber.*, **30**, 482 (1897); H. Eichwede and A. Skita, *Ann.*, **366**, 131 (1909).

[18] *Cf.* the separation of the enol and keto tautomers of ethyl acetoacetate, K. H. Meyer and V. Schoeller, *Ber.*, **53**, 1410 (1920).

[19] A. Lapworth, *Proc. Chem. Soc.*, **16**, 132 (1900); H. Meerwein, *Ann.*, **358**, 71 (1908); W. S. Johnson, J. Szmuszkovicz, C. R. Rogier, H. I. Hodler, and H. Wynberg, *J. Amer. Chem. Soc.*, **78**, 6285 (1956).

[20] G. B. Payne, *J. Org. Chem.*, **24**, 1830 (1959); F. Tiemann and P. Kruger, *Ber.*, **28**, 2121 (1895).

[21] C. W. T. Hussey and A. R. Pinder, *J. Chem. Soc.*, 3525 (1961); M. E. McEntree and A. R. Pinder, *ibid.*, 4419 (1957).

[22] O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923); C. H. DePuy and R. W. King, *Chem. Rev.*, 431 (1960).

[23] R. Morgan, *J. Chem. Soc.*, 754 (1924).

[24] A. W. Johnson, E. Markham, R. Price, and K. B. Shaw, *J. Chem. Soc.*, 4254 (1958).

partially freed from acetic acid by distillation at 31° (0.3 mm). The nmr spectrum of **11** in carbon tetrachloride showed two singlets at δ 2.32 and 6.30 with integrated intensities of 3:1, as expected. The high-resolution mass spectrum was obtained on a sample immediately after distillation and showed a molecular ion of mass 112.05241; calcd 112.05243. However, attempts to prepare samples for conventional analysis invariably led to polymerized material.

Adduct, 3, $(CH_3O)_3P$·Isopropylideneacetylacetone. Trimethylphosphite (0.6 g) was added to a frozen solution of isopropylideneacetylacetone (0.6 g) in 0.5 g of benzene. The mixture was warmed slowly under argon from −70 to +60°, and maintained at this temperature for 3 days. The benzene solution was then triturated three times with hexane. The resulting white crystals were recrystallized 3 times from hexane to yield 0.5 g of **3**, mp 58.5–61°. The structure was confirmed by nmr (Figure 1). The major ir bands are found at 3020 (sh), 2980 (m), 2850 (m), 1660 (s), 1590 (s), and 1450 (s) cm^{-1}.

Adduct, 4, $C_6H_5P(OCH_3)_2$·isopropylideneacetylacetone, was prepared in the same way as for **3**, from dimethyl phenylphosphonite and isopropylideneacetylacetone. Work-up yielded white crystals, mp 76–81°, with major ir bands at 3100 (sh), 3010 (sh), 2970 (m), 2860 (w), 1630 (s), and 1580 (s) cm^{-1}. The structure was confirmed by nmr (Figure 2).

Adduct, 5, $C_6H_5P(OCH_3)_2$·Methyleneacetylacetone. One equivalent of dimethyl phenylphosphonite was added to a freshly distilled sample of methyleneacetylacetone (0.5 g; 80% pure) in 5 ml of hexane. The solution was stirred and allowed to stand under argon for 2 hr at room temperature. The solid that formed was triturated with hexane and recrystallized from carbon tetrachloride–hexane (1:3); the resulting white crystals melted at 102–105° and showed major ir bands at 3090 (sh), 2950 (m), 2850 (w), 1650 (s), 1560 (s), 1350 (s), 1190 (s), 1080 (s), and 1040 (s) cm^{-1}.

The nmr spectrum at 100 Mc of the adduct **5** of dimethyl phenylphosphinite and methyleneacetylacetone at 30° in methylene chloride-d_2 consists of a singlet at δ 2.18 (6 H), attributed to the two methyl groups of the acetylacetone system, a doublet at δ 3.19 (2 H) with J_{H-P} = 17.5 cps attributed to the protons of the α-methylene group, a doublet at δ 3.43 (6 H) with J_{H-P} = 11.4 cps attributed to the six protons of the methoxyl groups, and a broad multiplet at δ 7.4–7.7 attributed to the five aromatic protons. At −63°, the signals from the protons of the methoxyl groups coalesce into a broad peak with a half-width of *ca.* 95 cps. When the sample is further cooled to −93°, two doublets at δ 3.04 with J_{H-P} = 9.6 cps and δ 3.84 with J_{H-P} = 12.6 are observed, although the signals are partially obscured by overlap with the signals from the methylene group. The high-temperature process (opening and closing of the ring, *via* a zwitterionic intermediate) cannot be observed because of the unfortunate accidental coincidence of the signals from the two methyl groups.

Adduct, 6, $P(OCH_3)_3$·Methyl Vinyl Ketone. Redistilled Aldrich methyl vinyl ketone (9.85 g) and trimethyl phosphite (16.25 g) were heated together under nitrogen at 45° for 48 hr. The product, **6**, (11 g) distilled at 56–57° (3 mm); principal ir bands at 2950 (m), 2860 (w), 1670 (s), 1450 (m), 1310 (s), 1180 (dbl, s), 1090 (s), and 1050 (s) cm^{-1}. Its nmr spectrum is shown in Figure 3.

Adduct, 7, $C_6H_5P(OCH_3)_2$·Methyl Isopropylideneacetoacetate. Methyl 3-isopropylideneacetoacetate[17] (1.8 g) was added under argon at 0° to a hexane solution of 1 equiv of dimethyl phenylphosphonite. After 24 hr the resulting white crystals were washed with hexane and recrystallized from carbon tetrachloride–hexane (1:1). The compound melted at 77–78.5°; principal ir bands at 3080 (sh), 2010 (sh), 2980 (m), 2860 (w), 1690 (s), 1600 (s), 1300 (s), and 1060 (dbl, s) cm^{-1}. The nmr spectrum in bromobenzene indicates that, at room temperature, the molecule is frozen in the conformation shown (structure **7**). The signal from the *gem* dimethyl group appears as two doublets, one centered at δ 1.84 with J_{H-P} = 21.2, and one centered at δ 1.76 with J_{H-P} = 19.5. The signal for the C-methyl group appears at δ 2.18 and that for the methyl ester group at δ 3.57. The signals for the apical and equatorial methoxyl groups appear at δ 3.06, J_{H-P} = 9.5 and at δ 3.7 with J_{H-P} = 12 (approximately), respectively. (The upfield peak from the equatorial methoxyl group is coincident with the signal from the ester methoxyl group.) At 39° the signals from the protons of the isopropylidene groups coalesce and at 62° the signals from the apical and equatorial methoxyl groups coalesce. (The difference in temperature for coalescence is related to the difference in chemical shift for the signals; see Discussion). At 100° the compound undergoes decomposition; the nmr spectrum appears however to be that expected for a rapidly pseudorotating phosphorane.

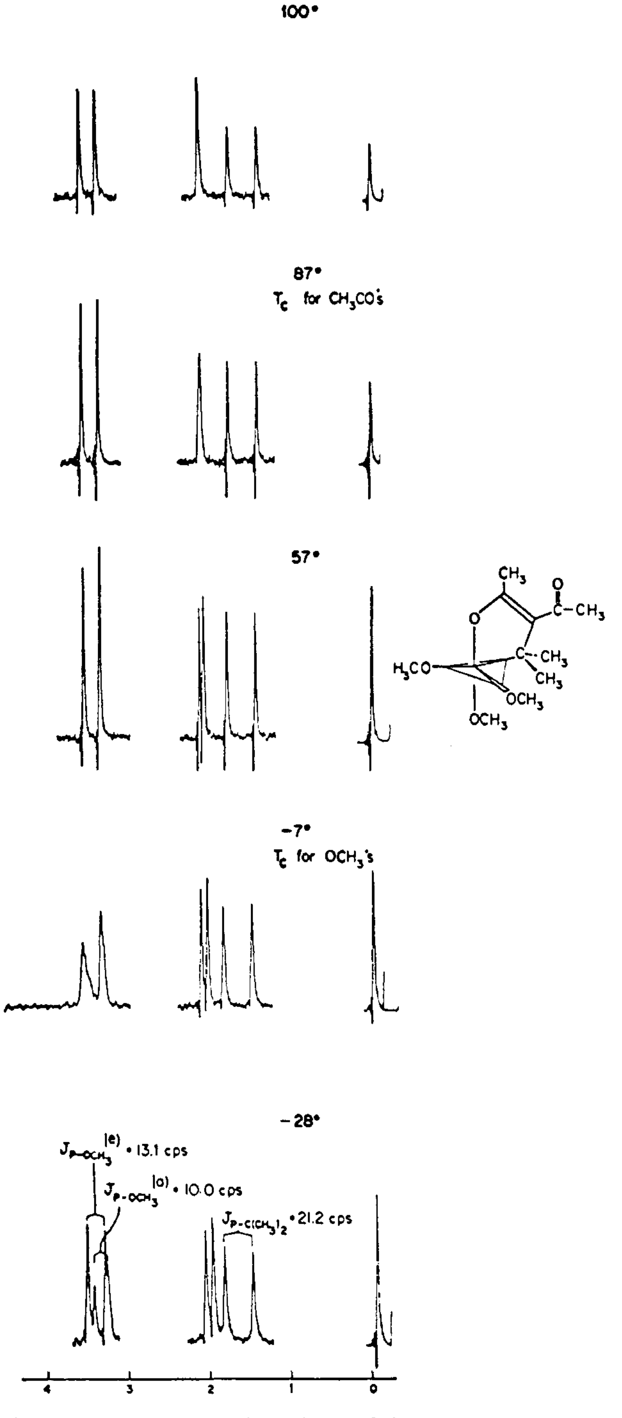

Figure 1. Temperature dependence of the nmr spectrum of the adduct **3** of trimethyl phosphite and isopropylideneacetylacetone (60 Mc; bromobenzene as solvent).

Adduct, 8, $C_6H_5OP(OCH_3)_2$·Benzylideneacetylacetone. A mixture of 5.0 g of dimethyl phenyl phosphite[25] and 5.0 g of benzylideneacetylacetone in 20 ml of benzene–hexane (1:4) was stirred and allowed to stand overnight at 40° under argon. The resulting crystals were triturated with hexane and recrystallized from toluene to yield white crystals (7 g) melting at 129–131°; principal ir bands are at 3030 (w), 2980 (m), 2850 (w), 1660 (s), 1570 (s), 1480 (s), 1220 (s), and 1080 (s) cm^{-1}. The nmr spectra are shown in Figure 4.

Adduct, 9, $(C_6H_5)_2POC_2H_5$·2(*p*-Nitrobenzaldehyde). The preparative method was adapted from that of Ramirez, *et al.*,[26] for the

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(25) A. E. Arbuzov and L. V. Nesterov, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 427 (1954).

(26) F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, **23**, 2067 (1967).

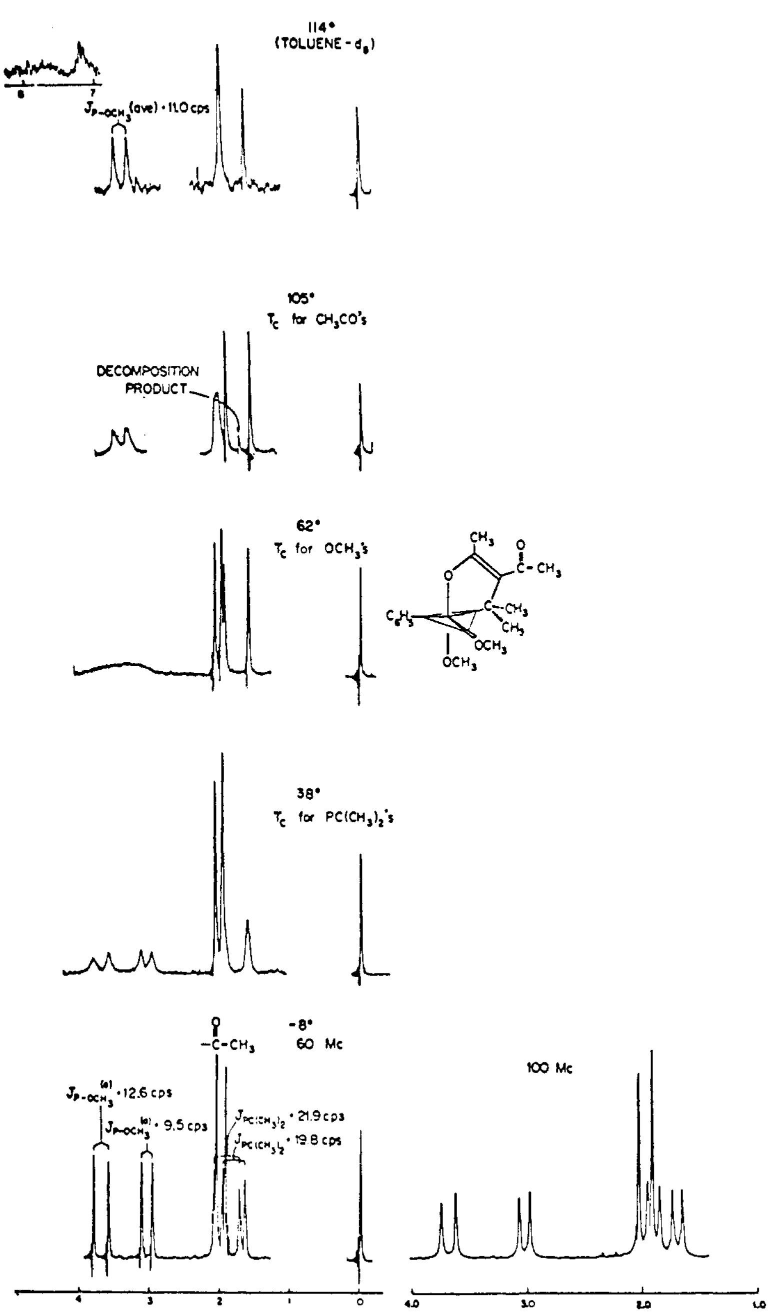

Figure 2. Temperature dependence of the nmr spectrum of the adduct **4** of dimethyl phenylphosphonite and isopropylideneacetylacetone (60 Mc except where otherwise indicated; bromobenzene as solvent except where otherwise indicated).

corresponding monophenyl derivative. Ethyl diphenylphosphinite[27] (1.8 g) was stirred under argon at 0° with 1.6 equiv of *p*-nitrobenzaldehyde in 30 ml of methylene chloride. The methylene chloride was removed by evaporation and the mixture (presumably *meso* and *dl* isomers) recrystallized from 1:3 methylene chloride-hexane. One pure isomer (of unknown stereochemistry) was obtained with mp 164–167°; principal ir bands at 3040 (w), 2980 (w), 1600 (m), 1520 (s), (1340 (s), 1260 (s), 1105 (m), 1070 (s), and 1040 (s) cm^{-1}. The compound was identified by its nmr spectrum, Figure 5.

Methods

Nmr Measurements. The nmr spectra were obtained with a Varian A-60 or Varian HA-100 nuclear magnetic resonance spectrometer equipped in each case with a Varian V-6031 B variable temperature probe. Although some decomposition occurred at high temperatures, the amount was usually small, and the original spectra (allowing for the signals from the impurities) were reproduced when the temperature was lowered.

High-Temperature Chemistry. The dissociation and recombination reaction was observed by mixing an adduct with one of the components for the preparation of an alternative adduct. For example, the adduct of dimethyl phenylphosphonite with isopropylideneacetylacetone was mixed with benzylideneacetylacetone, whereas the adduct of dimethyl phenyl phosphite and benzylideneacetylacetone was mixed with trimethyl phosphite. The reaction mixtures were heated for specified lengths of time in a high-temperature thermostat, cooled, and analyzed by nmr spectroscopy. In order to determine the kinetic order of the reaction, the components were mixed in various proportions in bromobenzene as solvent.

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(27) B. A. Arbuzov, *J. Russ. Phys. Chem. Soc.*, 42, 395 (1910).

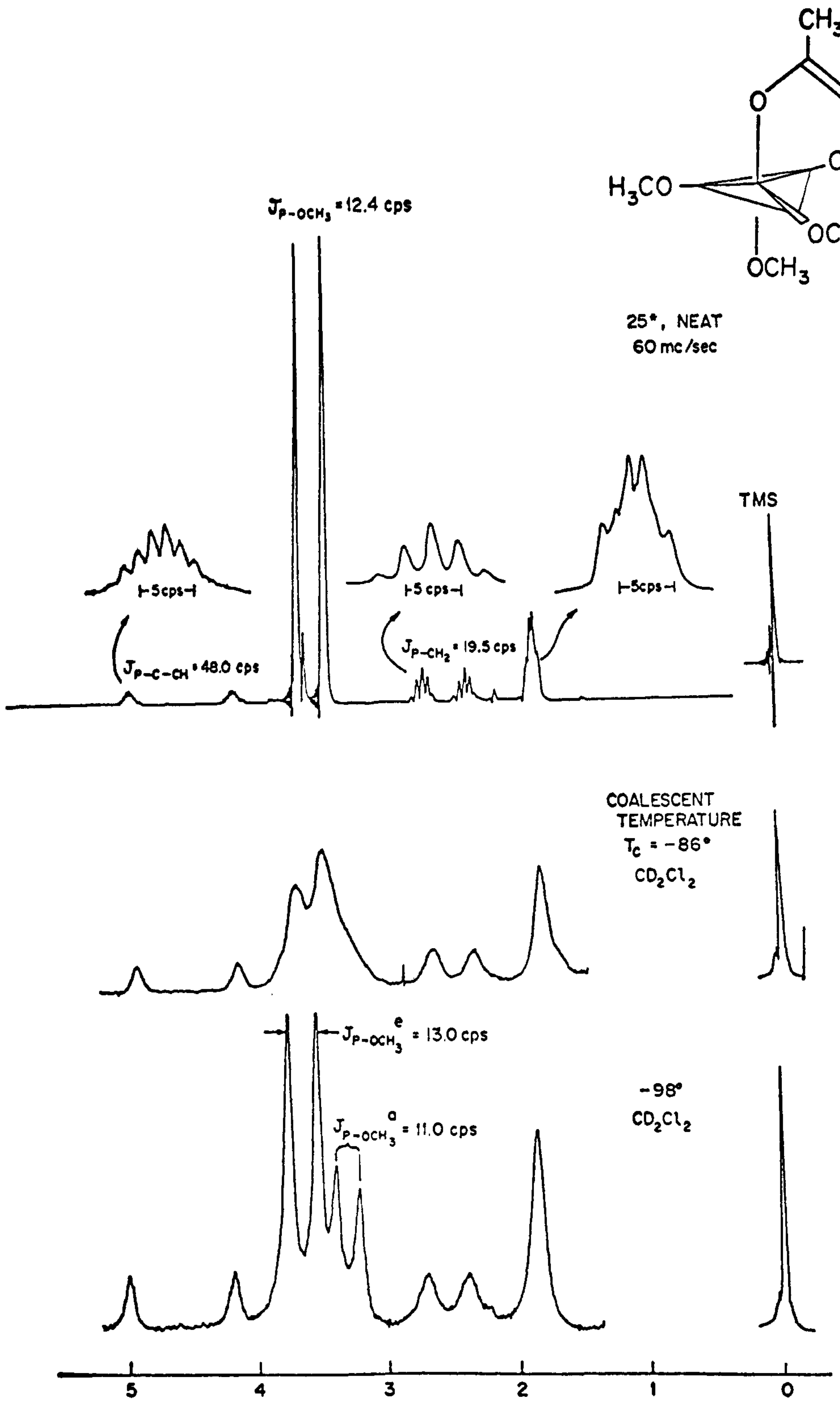

Figure 3. Temperature dependence of the nmr spectrum of the adduct 6 of trimethyl phosphite and methyl vinyl ketone (60 Mc; solvents as shown).

Other Measurements. Ir spectra were determined with a Perkin-Elmer Infracord. Analyses, performed by the Galbraith Analytical Lab., are recorded in Table I.

Results and Discussion

Pseudorotation. Alkyloxyphosphoranes that contain a five-membered ring are formed in accord with two rules: (1) alkyl groups preferentially occupy equatorial positions, while oxygen atoms preferentially occupy apical positions and (2) five-membered rings preferentially occupy one apical and one equatorial position, so as to minimize ring strain. At low temperatures, phosphoranes are frozen on the nmr time scale into structures that accord with these preference rules, but at higher temperatures (room temperature and

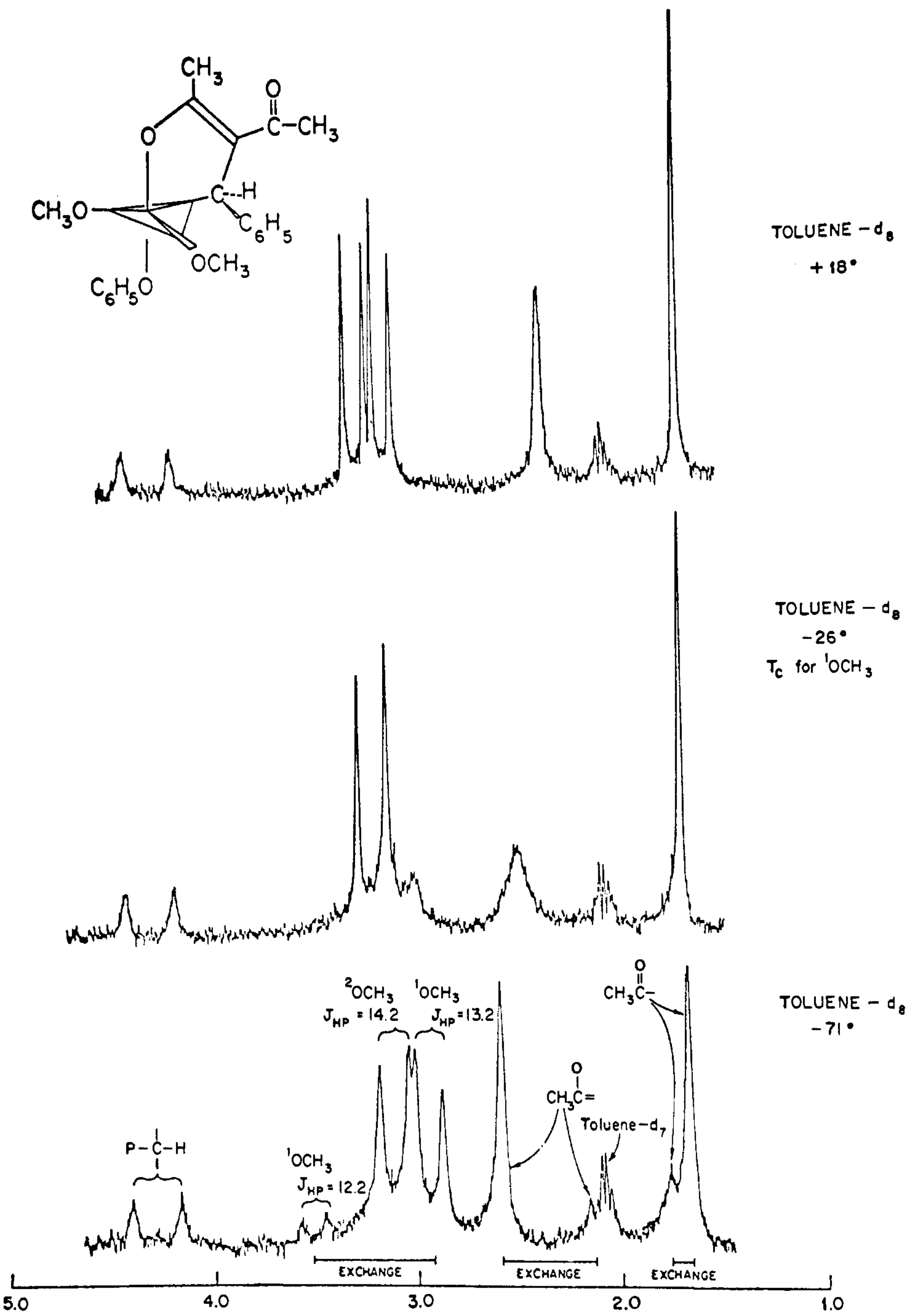

Figure 4. Temperature dependence of the nmr spectrum of the adduct **8** of dimethyl phenyl phosphite and benzylideneacetylacetone (100 Mc). The highest temperature measurements have been omitted because of incursion of peaks due to decomposition. The signals that mix because of exchange of the methoxyl or methyl groups are indicated in the spectrum for the lowest temperature.

somewhat above) the structures are rearranged so that some (but not all) of the groups attached to phosphorus become equivalent on an nmr scale. The theory of pseudorotation accounts both for the equilibrations that do and for those that do not occur. Two possible alternative processes (ring opening–reclosing and dissociation–recombination) occur at much higher temperatures, but have quite different consequences, predicted and observed, with respect to the nmr spectra of phosphoranes.

In order for pseudorotation to occur, thermal energy must be supplied so as to override the barriers to pseudorotation that are imposed either by the strain rule or by the Muetterties polarity rule or by both. This paper and the subsequent one[28] are concerned with the magnitude of the energy required to override these barriers to pseudorotation.

Our experiments have all been interpreted in terms of the Berry mechanism, discussed in ref 10. However, it must be noted that the data so far available do not unambiguously establish this mechanism. In particular, one of the alternatives suggested by Muetterties[29] for exchange of groups in trigonal-bipyramidal structures can also account for the nmr data. The process in question (Scheme IV of ref 29) holds one equatorial and one apical group fixed, while the other three groups are

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(28) D. Gorenstein, *J. Amer. Chem. Soc.*, **92**, 644 (1970).

(29) E. L. Muetterties, *ibid.*, **91**, 1636 (1969).

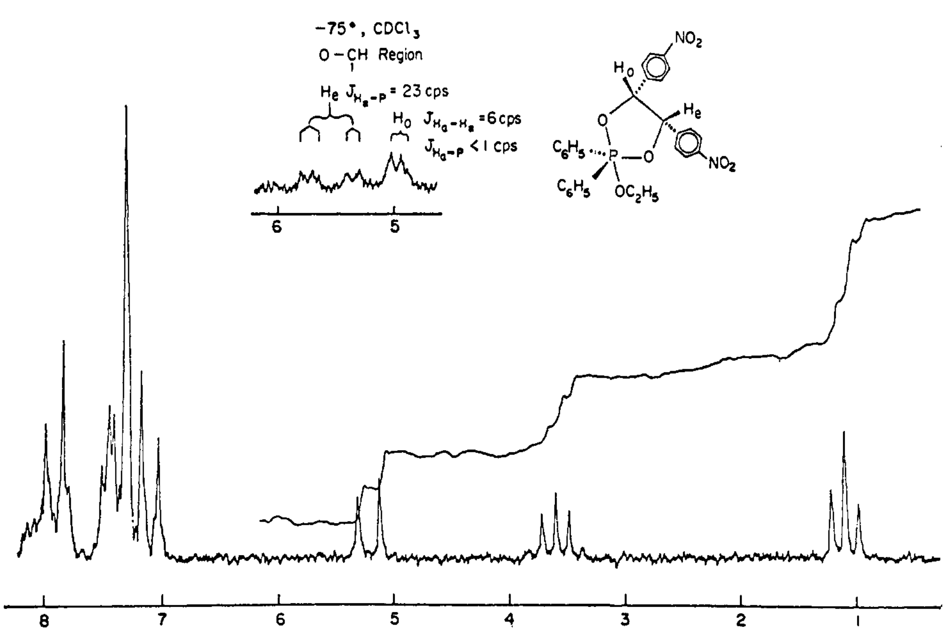

Figure 5. Temperature dependence of the nmr spectrum of the adduct 9 of ethyl diphenylphosphinite and 2 molar equiv of *p*-nitrobenzaldehyde (60 Mc).

interchanged by a threefold screw motion. However, this process if it is invoked at all, cannot completely replace pseudorotation, but must be assumed to supplement it. Although a consistent scheme can be evolved that includes this process, it seems simpler, at least for the present, to explain all the data in terms of pseudorotation.

The complete equilibration of the methoxyl groups in 1 at room temperature can be accounted for by overriding the barrier imposed by the Muetterties polarity rule. By contrast, it is not possible to account for the nmr spectra at moderate temperatures by overriding only the barrier to placing the five-membered ring in diequatorial positions. If an alkyl substituent in 1 could not occupy an apical position, the compound could only shuttle back and forth (as required by the Berry pseudorotation scheme) between the two structures shown below.

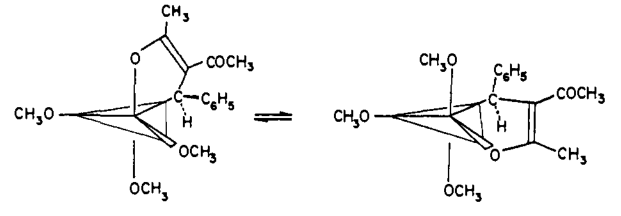

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Table I

No.	Compound	Molecular formula	Calculated C	Calculated H	Calculated P	Found C	Found H	Found P
3	$(CH_3O)_3P$·3-isopropylideneacetylacetone	$C_{11}H_{21}O_5P$	50.00	8.01	11.72	49.63	7.92	11.50
4	$C_6H_5(CH_3O)_2P$·3-isopropylideneacetylacetone	$C_{16}H_{23}O_4P$	61.93	7.47	9.98	62.18	7.46	9.78
5	$C_6H_5(CH_3O)_2P$·3-methyleneacetylacetone	$C_{14}H_{19}O_4P$	59.57	6.78	10.98	59.63	6.84	10.84
6	$(CH_3O)_3P$·methyl vinyl ketone	$C_7H_{15}O_4P$	43.28	7.79	15.95	42.94	7.71	15.98
7	$C_6H_5(CH_3O)_2P$·methyl 3-isopropylidene-acetoacetate	$C_{16}H_{23}O_5P$	58.87	7.11	9.50	58.96	7.29	9.32
8	$C_6H_5OP(OCH_3)_2$·benzylideneacetylacetone	$C_{20}H_{23}O_5P$	64.17	6.19	8.27	64.31	6.13	8.11
9	$(C_6H_5)_2(C_2H_5O)P$·2(*p*-nitrobenzaldehyde)[a]	$C_{28}H_{25}N_2O_7P$	63.14	4.73	5.82	63.35	4.82	6.09
10	3-Isopropylideneacetylacetone	$C_8H_{12}O_2$	68.53	8.64		68.74	8.53	
12	3-Isopropyl-3-acetoxyacetylacetone	$C_{10}H_{18}O_4$	60.00	8.06		60.01	8.36	
13	3-Methyl-3-acetoxyacetylacetone	$C_8H_{12}O_4$	55.83	7.03		55.96	7.19	

[a] *Anal.* Calcd: N, 5.26. Found: N, 6.11.

This would not result in mixing the methoxyl groups. Therefore pseudorotation *must* require overriding the barrier to apical carbon atoms. Further, this is a sufficient condition, since complete equilibration of the methoxyl groups of 1 can occur even if the strain rule is strictly obeyed (see below).

Strain Rule. Although the argument given above clearly demonstrates that one must be able to override the barrier to apical carbon atoms, and although it shows that one need not necessarily place the ring in

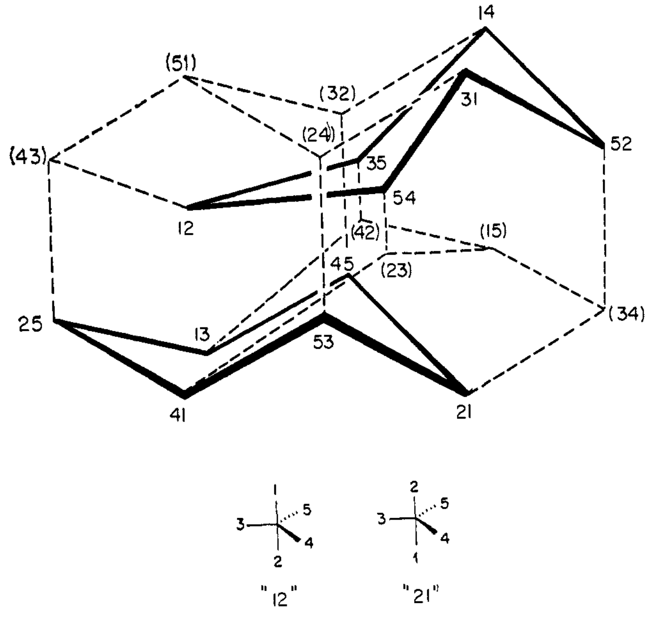


Figure 6. Topological diagram, according to Professor D. Cram, showing the interrelationship of the pseudorotamers of compound **2**. The schematic formulas at the bottom of the figure indicate the structures of two isomers with inversion of configuration at the phosphorus atom. The isomers designated by numbers in parentheses on the topological diagram are forbidden by the strain rule. The heavy lines show the pathways for pseudorotation that interconnect the remaining isomers including some where alkyl or aryl groups are in apical positions. No allowed pathway interconverts any two members of the independent sets of six pseudorotamers connected by the heavy lines.

diequatorial positions, the argument so far presented does not prove that the pseudorotation process does not proceed through overriding *both* barriers.

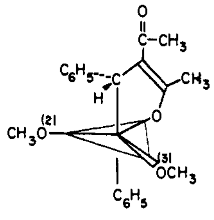
Some further restraint on the system is imposed by the observation, discussed in the introductory statement, that, even at high temperatures, the two methoxyl groups of **2** do not equilibrate completely. In order to equilibrate these groups without destroying the structure of **2**, epimerization must occur at phosphorus. Otherwise, although the *cis* and *trans* isomers of **2** are interconverted by a pseudorotation process, the equatorial (starred) methoxyl group of *cis*-**2** is equilibrated only with the apical (starred) methoxyl group of *trans*-**2**, and *vice versa*. These patterns were pointed out in the prior publications,[3,5] and can be developed by writing out the pseudorotation processes in detail.

Formalized Pseudorotation. A more convenient method of following a series of pseudorotations has been formalized by Muetterties,[29,30] by Dunitz and Prelog,[31] by Lauterbur and Ramirez,[32] and by Cram.[33] (An earlier equivalent representation, developed for a quite different problem, was put forth by Balaban, D. Fărcaşiu, and Bănică.[34]) These authors all offer diagrams where each apex represents an isomeric phosphorane, and the line connecting any two of them represent a pseudorotation process.

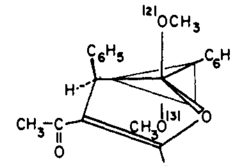
We have chosen Cram's diagram as the most convenient for the purpose of highlighting the pathways leading to epimerization. In Figure 6, each isomer of a trigonal-bipyramidal compound of pentacovalent phosphorus is designated by the numbers of its apical substituents, naming the upper one first; the other three substituents are assumed to be arranged counterclockwise in equatorial positions.

For compound **2**, we number the oxygen atom in the ring as **1**, the carbon of the ring as **5**, and the phenyl group as **4**. Then "**15**" (and "**51**") represent isomers that could never be formed, since they require the ring to occupy two apical positions. If we assume further that the strain rule is inviolate, then the isomers indicated in parentheses in Figure 6 cannot be formed, and the diagram reduces to the isomers and processes shown in heavy type. The diagram breaks cleanly into two six-membered cycles, but there is no path by which one can get from one to the other. Passage from one cycle to the other is required to effect an epimerization about phosphorus, since only in this way can one convert isomer "**12**" to "**21**", or "**35**" to "**53**", etc.

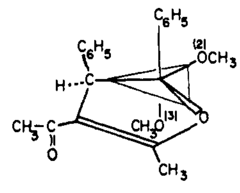
Detailed examination of Figure 6 shows that none of the pathways from one epimer to the other is allowed. In particular, the pathway *via* the isomer "**42**" or the one *via* "**43**" (*via* their epimers "**24**" or "**34**") demands the formation of a structure that simultaneously breaks the polarity and strain rules; it is therefore understandable that these processes do not occur. When these intermediates are eliminated from consideration, then a path from "**12**" to "**21**" in Figure 6 will require passing successively through the intermediates "**54**" and "**23**" (or through their epimers "**45**" and "**32**"). Since the methoxyl groups of **2** do not become completely equivalent, even at high temperatures, either the structure "**54**" or the structure "**23**" (or both of them) must be of high energy.



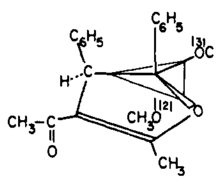
"54"



"23"



"43"



"42"

The phosphorane **8** was specifically designed and synthesized to obtain further information bearing on the possibility of epimerization about the phosphorus atom. This compound has the same symmetry as **2**, but differs from it in that a phenoxyl group rather than a phenyl group is attached to phosphorus. Thus for **8**, in the isomers "**54**", "**24**", and "**34**", a phenoxyl group rather than a phenyl group occupies one of the apical positions.

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(30) E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967); E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968).

(31) J. D. Dunitz and V. Prelog, *Angew Chem. Intern. Ed. Engl.*, **7**, 725 (1968).

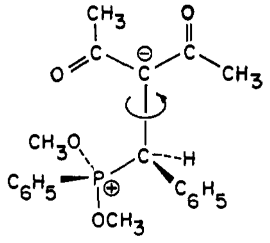
(32) F. C. Lauterbur and F. Ramirez, *J. Amer. Chem. Soc.*, **90**, 6722 (1968).

(33) D. Cram, private communication. Professor Cram informed the authors that his diagram was inspired by that of Dunitz and Prelog.

(34) A. T. Balaban, D. Fărcasiu, and R. Bănică, *Rev. Roum. Chim.*, **11**, 1205 (1966).

A detailed consideration of Figure 6 then shows that, for **8**, the methoxyl groups can become equivalent provided that the five-membered ring can be placed in diequatorial positions.

Before discussing the nmr spectrum of **8**, it is necessary to recall the spectrum, and particularly the high-temperature spectrum of **2**. At 120–160°, the signals from the two methyl groups of the acetylacetone system first coalesce and then sharpen to a singlet. This behavior has been ascribed to the opening and closing of the five-membered ring, through the zwitterionic structure shown below, with concomitant rotation about a carbon–carbon bond. Rotation about this carbon–carbon bond cannot cause epimerization at phosphorus and so cannot make the methoxyl groups nmr equivalent; the starred and unstarred methoxyl groups of **2** give different nmr signals even at 160°.



The nmr spectrum of **8**, the adduct of dimethyl phenyl phosphite and benzylidene acetylacetone, is shown in Figure 4. At low temperatures, three isomers (a compound with the phenoxyl group apical, and *cis* and *trans* isomers with the phenoxyl group equatorial) should be formed; two of them are observed. On raising the temperature to about 30° where the fast exchange limit of pseudorotation, on the nmr time scale, begins, a spectrum is obtained that resembles that for **2**, in that the two methoxyl groups do not become completely equivalent; reference to the Cram diagram, Figure 6, shows that this is the result expected if, at moderate temperatures, the strain rule is obeyed. However, when the temperature is raised to 140°, the signals for the methoxyl groups coalesce, and at higher temperatures the signal from them sharpens to a doublet, with J_{H-P} = 12.7 cps. The methyl groups of the acetylacetone system do not become equivalent at the same temperature, but the activation energies for coalescence of the methyl and methoxyl groups are about the same. The detailed treatment for this and other examples, treated qualitatively in this paper, are presented elsewhere.[28]

Since the methoxyl groups do become equivalent at high temperatures for **8**, it appears possible that the high energy process forces the five-membered ring into a diequatorial conformation. The energy required to do so, however, exceeds that required to override the barrier to placing an alkyl or aryl substituent in an apical position.

Dissociation of the adduct to starting materials, and recombination, could, in principle, provide an alternative mechanism for equilibration of the methoxyl groups. This process occurs, but only slowly. For example, when the adduct, dimethyl phenylphosphonite·isopropylideneacetylacetone is heated with benzylideneacetylacetone, the reaction produces the adduct, dimethyl phenylphosphonite·benzylideneacetylacetone, and releases isopropylideneacetylacetone. The reaction is first order in the original adduct, with a half-time of 24 min at 110°; the rate is independent of the concentration of benzylideneacetylacetone. Other adducts react at comparable or smaller rates. Thus the dissociation–recombination process is too slow to be of significance on the nmr time scale at the temperatures of this investigation.

Asymmetry in the Ring. In the previous discussion[2] of the nmr spectrum of **1**, we pointed out that at low temperatures there are three different kinds of methoxyl groups because of the asymmetry at the tetrahedral carbon atom of the ring, and that in **2**, the methoxyl groups never became equivalent[3] both because of the constraints on pseudorotation and because of the asymmetry of this carbon atom. The theory can be tested by studying the nmr spectra of compounds where this asymmetry is lifted. Phosphoranes prepared from isopropylidene acetylacetone and from methylene acetylacetone serve this purpose.

The nmr spectrum of the adduct **3** of trimethyl phosphite and isopropylideneacetylacetone at various temperatures is shown in Figure 1. At low temperatures the compound, as predicted, shows nmr signals (doublets) from two kinds of methoxyl groups in the ratio 2:1 (equatorial–apical); at temperatures around 60° where pseudorotation occurs, it shows only one sharp doublet, as predicted. The signal for the *gem*-dimethyl groups is also a doublet, with $J_{P\text{-}C(CH_3)_2}$ = 21.4 cps; this is a reasonable value for the coupling of a phosphorus atom to β hydrogen atoms.[35] The two methyl groups of the acetylacetone system show a coalescence temperature of 87°, which is 80° higher than that for the methoxyl signals, although the chemical shift is similar. Thus the nmr spectrum demonstrates that two different processes occur with **3**. This second process is presumably ring opening and closing.

The nmr spectrum of the adduct **4** of dimethyl phenylphosphonite and isopropylideneacetylacetone is shown in Figure 2. At low temperatures, as predicted, the equatorial and the apical methoxyl groups each gives rise to only one doublet, as expected for a single isomer; the spectra thus confirm that the isomers observed in **2** arise because of the asymmetry at the tetrahedral carbon atom of the ring. The *gem* dimethyl group gives rise, however, to two separate doublets, since one of these methyl groups is *cis* and the other *trans* to the equatorial phenyl group. The coalescence temperature for the signals from the *gem* dimethyl groups is 38° and that for the methoxyl groups is 62°. The activation energies calculated[28] for these processes are, however, the same, as would be expected since they arise from the same pseudorotation; the difference in the temperatures at which coalescence occurs is related to the difference in the chemical shifts of the groups that are equilibrated.

An entirely similar explanation accounts for the spectrum of **5**, the condensation product of dimethyl phenylphosphonite and methyleneacetylacetone.

Ring Opening. The compounds **6** and **9** would not be expected to undergo ring opening as readily as **1**, **2**, **3**, **4**, and **5**, since on opening **6** would yield the anion of a simple enol and **9** would yield an alkoxide ion, whereas compounds **1–5** would yield resonance-stabilized anions related to the acetylacetone system. Yet the exchange

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(35) K. D. Bartle, R. S. Edmundson, and D. W. Jones, *Tetrahedron*, 1701 (1967).

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

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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

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[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).

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

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

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[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.