Inhibition of Positional Exchange in Derivatives of 2,2-Dihydro-1,4,2-dioxaphospholanes

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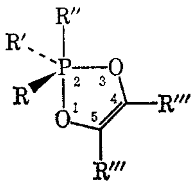
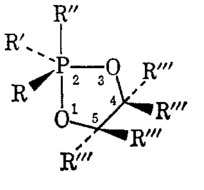
Trimethyl phosphite reacted with pentafluorobenzaldehyde at 0° in pentane and gave a crystalline mixture of *cis*- and *trans*-3,5-di(pentafluorophenyl)-2,2,2-trimethoxy-2,2-dihydro-1,4,2-dioxaphospholanes in a 55:45 proportion and in 85% of theory. The variable-temperature ^{1}H nmr spectrum of the *cis* isomer showed that the three methoxy groups on the trigonal bipyramidal pentavalent phosphorus underwent rapid intramolecular positional exchange in solutions above *ca.* −100°. This exchange was inhibited at about −110°. The spectrum at −130° showed the presence of two methoxy groups in nonequivalent equatorial positions and one methoxy group in an apical position. The phospholane ring occupied the remaining apical–equatorial positions. The interconversions among the possible stereoisomeric trigonal bipyramids by pseudorotation are discussed. ^{31}P nmr data are given.

The structure of a cyclic *oxyphosphorane* (1) was elucidated by X-ray analysis.[2] Variable-temperature ^{1}H nmr and ^{31}P nmr spectroscopy showed that the groups attached to the trigonal bipyramidal phosphorus underwent rapid intramolecular positional exchange in solutions above *ca.* −80°.[3] The same conclusion was reached[4] for certain derivatives of structure 2.

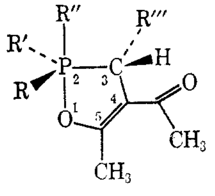


1

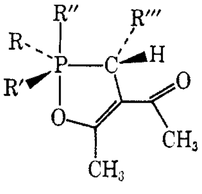


2

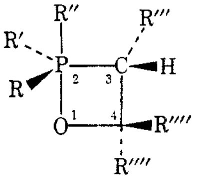
The positional exchange of the groups on phosphorus in compounds of type 3–6 was inhibited below certain temperatures.[3–5] Pairs of diastereomers of a given oxyphosphorane, 3–4 and 5–6, were detected at 30°; stereomutation among these diastereomers was observed above certain temperatures. (To avoid confusion, diastereomers differing in the configuration at *phosphorus* will be called *syn* and *anti*. Those differing in the configuration at *carbon* exclusively will be called *cis* and *trans*.)



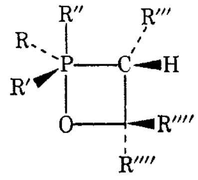
3, *anti*-R/R'''



4, *syn*-R/R'''



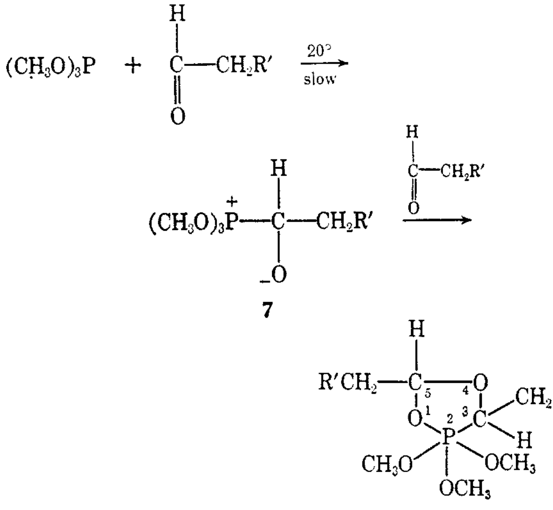
5, *anti*-R/R'''



6, *syn*-R/R'''

It was concluded[3–5] that these positional exchanges of groups in the phosphoranes could occur by different mechanisms depending on the temperature and on the stability of the compounds: (1) a bond-bending process which has been called "pseudorotation"[6] or "polyhedral rearrangement;"[7] (2) an intramolecular P–O bond rupture and recombination.

This paper is concerned with the dynamic stereochemistry[8] of derivatives of the 2,2-dihydro-1,4,2-dioxaphospholanes; *e.g.*, 8 and 9. Oxyphosphoranes of this type have been made from the reaction of unsubstituted aliphatic monoaldehydes with trialkyl phosphites.[9] However, the products were liquid mixtures of two diastereomers *at carbon* which could not be separated by distillation. Their ^{1}H nmr spectra were



8, *cis*-H/H; δ^{31}P = +32.8 ppm *vs.* H_3PO_4

9, *trans*-H/H; δ^{31}P = +34.8 ppm

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[1] John Simon Guggenheim Fellow, 1968. This work was supported by grants from the Public Health Service (CA-04769) and the National Science Foundation (GP-6690).

[2] W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 2268 (1967).

[3] (a) F. Ramirez, *Trans. N. Y. Acad. Sci.*, **30**, 410 (1968); (b) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

[4] (a) F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, **33**, 3787 (1968); (b) F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, **90**, 6726 (1968).

[5] For other reports of the variable-temperature ^{1}H nmr spectrum of **3**, see F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

[6] (a) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); (b) R. R. Holmes and R. M. Deiters, *J. Amer. Chem. Soc.*, **90**, 5021 (1968).

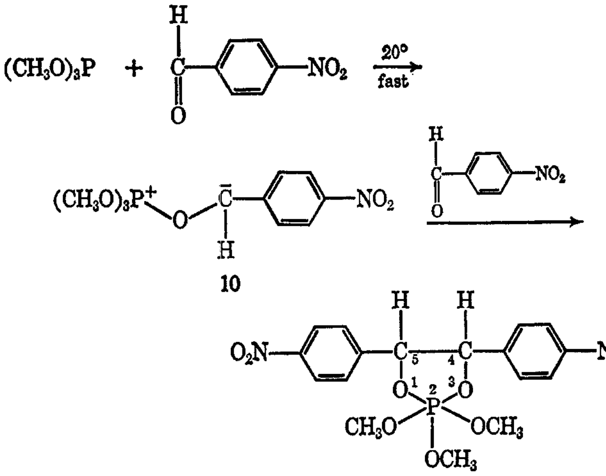
[7] (a) E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967); (b) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); (c) E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968).

[8] (a) K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. I, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, Chapter I; (b) M. Van Gorkom and G. E. Hall, *Quart. Rev.* (London), **22**, 14 (1968); (c) J. E. Anderson, *ibid.*, **19**, 426 (1965); (d) L. H. Sommer, "Stereochemistry Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

[9] (a) F. Ramirez, A. V. Patwardhan, and S. R. Heller, *J. Amer. Chem. Soc.*, **86**, 514 (1964); (b) F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Org. Chem.*, **33**, 13 (1968); (c) F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, **23**, 2067 (1967).

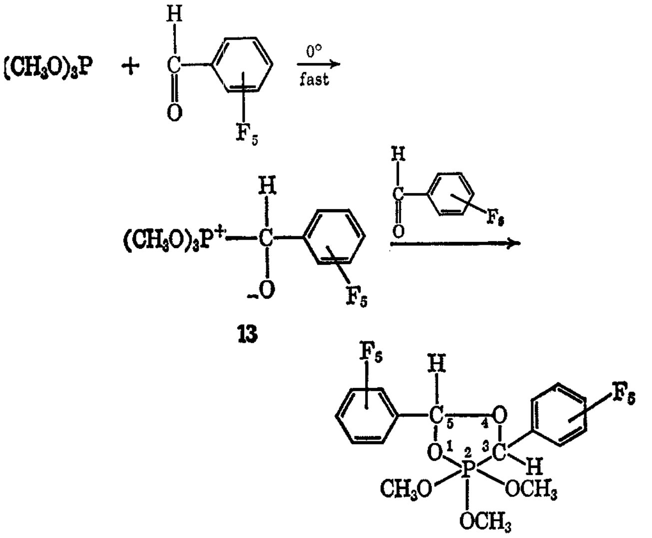
complex and unsuitable for the variable-temperature studies.

Attempts to prepare 1,4,2-dioxaphospholanes from the reaction of *o*- and *p*-nitrobenzaldehydes with trialkyl phosphites led instead to derivatives of 2,2-dihydro-1,3,2-dioxaphospholanes,[9] **11** and **12**.



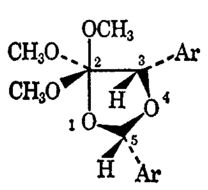
11, *cis*-H/H; $\delta^{31}P = +49.6$ ppm
12, *trans*-H/H; $\delta^{31}P = +50.2$ ppm

The type of product that can be obtained from a carbonyl compound and a trivalent phosphorus compound depends on the structure of both reactants and on the temperature at which these are allowed to react.[10] Therefore, we investigated the behavior of other aldehydes with several phosphite esters and found that the combination of pentafluorobenzaldehyde with trimethyl phosphite *at 0° in pentane solution*[11] was ideal for the purpose of this research.

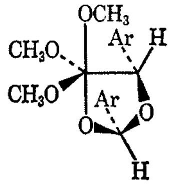


14, *cis*-H/H
15, *trans*-H/H

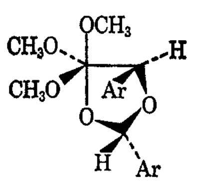
The crystalline mixture of 1,4,2-dioxaphospholanes **14** and **15** was obtained in 85% of the theory. The *cis*-H/H isomer **14** predominated (*ca.* 55:45 proportion) and could be isolated free from the *trans*-H/H isomer **15** by crystallization. The nmr data were readily interpreted, as shown in Table I. Note the value of the 3P shifts *vis-à-vis* those of related oxyphosphoranes[3,9] **8–9** and **11–12**. The nmr signals due to the ring protons of isomer **14** were at lower field than those of isomer **15**. The configurations were assigned with the aid of formulas **14-I**, **II** and **15-I**, **II**. The Roman numerals refer to two ring conformations for a given configuration. The phosphorus is placed at the center of a trigonal bipyramid and the phospholane ring in one of the apical–equatorial planes.[2-4] In **14-I** and **15-I**, the O-1, P-2, and C-3 atoms are in one plane, O-4 is below it, and O-5 is above it.[12] In **14-II** and **15-II**, the O-1, P-2, and C-3 atoms are in the plane, O-4 is above it, and C-5 is below it. The two ring protons come close to each other in **14-I**. A ring proton comes close to an aryl group in **15-I**. The proton shielding should be less effective in **14-I** (the *cis* isomer) than in **15-I** (the *trans* isomer).[2,9]



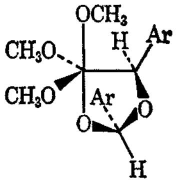
14-I, *cis*-H/H



14-II, *cis*-H/H



15-I, *trans*-H/H



15-II, *trans*-H/H

The coupling constants in Table I can be rationalized on the assumption that the molecules resemble conformations I rather than II. The H–P coupling of the C-5 H is rather small[3,9] in both isomers **14** and **15**. In conformations I the dihedral angle formed by the planes containing the atoms H–C-5–O-1 and P-2–O-1–C-5 is not very far from 90° where the H–P coupling should be at a minimum;[3,9] in conformations II that angle should be closer to 180°, where the H–P coupling should be at a maximum. The H–P coupling of the C-3 H is much larger in the *cis* **14** than in the *trans* **15** isomers. This may be related to the circumstance that the H–C-3 bond is nearly in the equatorial plane in **14-I**, but is reaching upwards away from the equatorial plane in **15-I**.

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[10] In general, products resulting from an attack by trivalent phosphorus on carbonyl *oxygen* are obtained when the carbonyl function is activated by electron-withdrawing substituents (including a second carbonyl group) due to the resulting stabilization of the negative charge on carbonyl carbon in the 1:1 adduct **10**. From some *aldehydes* of this type we have isolated products of carbon attack in low-temperature reactions, and products of oxygen attack in high-temperature reactions. From other aldehydes we have isolated only products of oxygen attack at all temperatures. From *ketones* of this type we have so far obtained exclusively the products of oxygen attack. The phosphorus compounds studied have been trialkyl phosphites, triaminophosphines, and trialkylphosphines. See ref 3 and 9 for pertinent literature.

[11] The reaction of pentafluorobenzaldehyde with trimethyl phosphite at 80° gave mostly *1,3,2-dioxaphospholanes* analogous to **11** and **12**. Small amounts of the *1,4,2-dioxaphospholanes*, **14** *and* **15**, and significant amounts of phosphonate and phosphate esters were also produced. *Cf.* F. Ramirez, J. F. Pilot, C. P. Smith, S. B. Bhatia, and A. S. Gulati, *Bull. Soc. Chim. Fr.*, in press.

[12] Note that in **14-I** the two aryl groups are far from each other *and* from the equatorial methoxy groups, while in **14-II** the two aryl groups are close to each other *and* to an equatorial methoxy. In both **15-I** and **15-II**, there is an aryl group close to a hydrogen *and* to one equatorial methoxy; however, that aryl is on C-3 in **15-I**, and on C-5 in **15-II**.

TABLE I

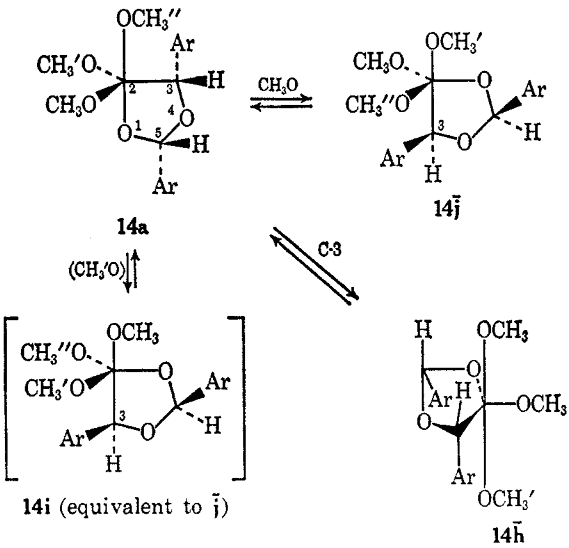
^{31}P AND ^{1}H NMR SIGNALS[a] OF *cis*- AND *trans*-3,5-DI(PENTAFLUOROPHENYL)-2,2,2-TRIMETHOXY-2,2-DIHYDRO-1,4,2-DIOXAPHOSHOLANES IN $CDCl_3$ AT 25°

	cis **14**	*trans* **15**
δ^{31}P	+34.1	+38.4
$\tau_{C\text{-}5\text{-}H}$	3.52	3.94
$J_{C\text{-}5\text{-}H\text{-}P}$	2.0	3.5
$\tau_{C\text{-}3\text{-}H}$	4.73	5.0
$J_{C\text{-}3\text{-}H\text{-}P}$	17.0	6.0
τ_{CH_3OP}	6.38	6.32
J_{CH_3OP}	12.8	12.8

[a] ^{31}P nmr signals in parts per million *vs.* $H_3PO_4{=}O$, measured at 40.5 Mcps. ^{1}H signals in parts per million *vs.* TMS = 10 (τ), measured at 60 Mcps. *J* in cycles per second.

The variable-temperature ^{1}H nmr spectrum of the *cis* **14** isomer is shown in Figure 1. *Clearly, the three methoxy groups on phosphorus were undergoing rapid positional exchange above −100°, but the exchange was inhibited at about*[13] *−110°*. At −135° the three methoxy groups were distinguishable. It is known[3] that methoxy groups in equatorial positions of related oxyphosphoranes give nmr signals at lower fields and with larger H–P coupling constants than methoxy groups in apical positions. Therefore, the spectra in Figure 1 justify the conclusion that *the stable form of this type of trigonal bipyramid had the phospholane ring in an apical–equatorial plane* as shown[14,15,15a] in formulas **14a** or **14j̄**, because in these isomers there are two equatorial and one apical methoxy groups. The remaining isomer, **14h̄**, with the ring in a diequatorial plane, must have two apical and one equatorial methoxy groups.[14,15]

Formula **14a** is favored over **14j̄** for the most stable bipyramid because in **a** the element of lower electronegativity (carbon) is equatorial, and in **j̄** it is apical.[2–7] Steric considerations[2–4] may also play an important role in the relative stability of **a** and **j̄**. The X-ray analysis of an oxyphosphorane of type **1** showed[2] that the trigonal bipyramid was very crowded due to several short nonbonded interactions. In particular, some of the atoms *directly attached* to the phosphorus were close to some of the atoms *once removed* from the phosphorus, for example, C-3 and the carbon of CH_3O in formula **14j̄**.



The positional exchange of the groups in **14** and **15**, and the inhibition of this exchange below −110°, can be explained by the mechanism of pseudorotation[3–7,15] (PR). Starting with isomer **14a**, three PR can be performed since there are three equatorial groups that can be used as pivot.[14–17] The three PR generate only two new diasteromers, **14j̄** and **14h̄**, because the third bipyramid, **14i**, is stereochemically equivalent to **14j̄**. Isomer **j̄** was assumed to have a higher energy than **a** due to the positions of the carbon and the oxygen atoms in the trigonal bipyramids. Isomer **h̄** is assumed to have a higher energy than **j̄** because in **h̄** the ring is in a diequatorial plane; molecular models and considerations of the nature of the bonding in trigonal bipyramidal pentacoordinated phosphorus[2,6–7] support this assumption. It is reasonable, therefore, that the energy barriers associated with the pseudorotation of **14a** ⇄ **14j̄** and of **14a** ⇄ **14h̄** are sufficiently high to permit inhibition of positional exchange at about −110°.

It can be verified[14–17] that a CH_3O group in a 1,4,2-dioxaphospholane of type **14** can be placed in nine different magnetic environments if all pseudorotations are allowed among bipyramids of the three diastereomeric types **14a**, **14j̄**, and **14h̄**. The CH_3O groups can be placed in six different magnetic environments if no bipyramid with a diequatorial ring, **14h̄**, is allowed. The bipyramids that can be drawn to arrive at these conclusions can be grouped into three sets, each set consisting of six stereochemically equivalent forms: **a**, **f**, **e**, **ē**, **f̄**, **ā**; **d**, **j**, **i**, **ī**, **j̄**, **d̄**; **b**, **h**, **c**, **c̄**, **h̄**, **b̄**.

If diequatorial-ring isomers are eliminated, **14h**, the last set is eliminated; in this case, there are only two sets of bipyramids with the interesting property that *interconversions by pseudorotations are possible within each set, but are forbidden among members of different sets*:[15] **14a** ⇄ **i** ⇄ **f̄** ⇄ **d** ⇄ **e** ⇄ **j̄** ⇄ **a**; **14ā** ⇄ **ī** ⇄ **f** ⇄ **d̄** ⇄ **ē** ⇄ **j** ⇄ **ā**. This analysis leads to the

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[13] Although coalescence of the methoxy doublet was not complete until *ca.* −110°, clear indications of changes in the signals were noticeable at about −70°. In contrast, the methoxy doublet (or the CH_3-P doublet) in the 1,3,2-dioxaphospholenes and phospholanes, **1** and **2**, remained essentially unchanged from 80 to −80°.

[14] The notation used here is described in ref 15. When the five groups in the trigonal bipyramid (P1,2) (3,4,5) are different but symmetrical, there are 20 stereoisomers, *i.e.*, 10 diastereomeric pairs of enantiomers. The 10 diastereomers are represented by the letters **a**, **b**, . . . , **j**; the enantiomers by **ā**, **b̄**, . . . , **j̄**. The letter sequence corresponds to the 10 possible permutations: (1,2)(3,4,5) = **a**; (1,3)(2,4,5) = **b**; (1,4)(2,3,5) = **c**; etc. In the 1,4,2-dioxaphospholanes made from trimethyl phosphite and pentafluorobenzaldehyde, two of the five groups are asymmetric; therefore, **a** and **ā** are no longer enantiomers. (To obtain **ā**, exchange the relative positions of CH_3O and $CH_3'O$ in **a**.) The number of stereoisomers is reduced because three groups on phosphorus are identical and symmetric (CH_3O). Bipyramids with the ring in two apical positions are forbidden because the ring cannot accommodate an ∠ O1-P2-C3 of 180°. This leads to 12 stereoisomers, *i.e.*, 6 diastereomers, of which 3 have the *cis*-H/H and 3 the *trans*-H/H configuration. Only the former **a**, **j̄**, and **h̄** are shown. The *trans* diastereomers can be visualized by exchanging the positions of H and Ar at C-3.

[15] P. C. Lauterbur and F. Ramirez, *J. Amer. Chem. Soc.*, **90**, 6722 (1968).

[15a] NOTE ADDED IN PROOF.—A scheme to display certain interconversions among carbonium ions, which resembles our scheme (ref 15) to display interconversions among trigonal bipyramidal phosphorus by pseudorotation, was described by A. T. Balaban, D. Farcasio, and R. Banica, *Rev. Roum. Chem.*, **11**, 1205 (1966). This paper was not available to us when the present manuscript was submitted. For other recent work, see E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969); J. Dunitz and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **7**, 725 (1968).

[16] To convert **a** into **j̄**, grasp CH_3O of **a**, push back two apical groups, and pull forward two equatorial groups. This gives **j̄** lying on its side; rotate it 90° counterclockwise around the pivot axis, CH_3O–P, and then turn it upside down (*i.e.*, rotate 180° around the O-1–P axis).

[17] To follow the movements of the methoxy groups these are given different labels, CH_3O CH_3O', and $CH_3''O$. Of course, those "isomers" will be *stereochemically equivalent* and will differ only in the relative positions of the labeled methoxy group on the bipyramid.

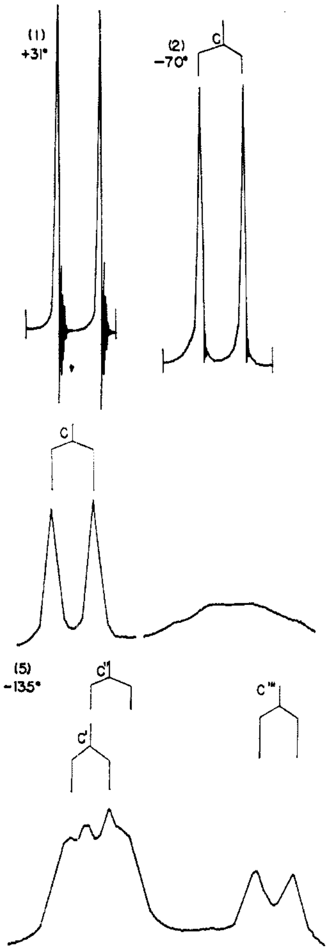
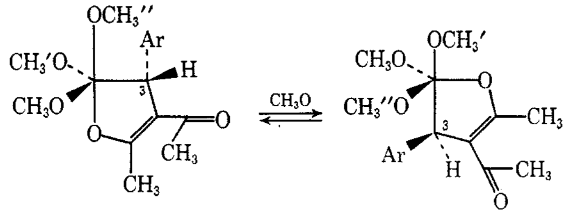


Figure 1.—Temperature dependence of ^{1}H nmr signals due to the CH_3O groups of *cis*-3,5-di(pentafluorophenyl)-2,2,2-trimethoxy-2,2-dihydro-1,4,2-dioxaphospholane, in parts per million *vs.* TMS = 10 (τ), in CF_2Cl_2, taken in the Varian HA-100D spectrometer. *Positional exchange of the three CH_3O groups* was evident in curves 1 at 31°, 2 at −70°, and 3 at −92°; τ 6.45, J_{HP} = 12.5 cps due to equatorial-apical CH_3O. *Coalescence* of the signal was observed in curve 4 at −110°; signal width = 65 cps. *A frozen trigonal bipyramid* was observed in curve 5 at −135°; τ 6.27, J_{HP} = 12.2 cps, and τ 6.33, J_{HP} = 12.9 cps, due to the CH_3O groups in equatorial positions; and τ 6.83, J_{HP} = 10.8 cps, due to the CH_3O group in apical position. No further change occurred, at −140°. Curves 1–4 are at the same spectral amplitude; curve 5 is at a different amplitude.

conclusion that, as long as pseudorotation occurs among **14a** and **14j̄**, the three CH_3O– groups will give one ^{1}H nmr signal, a doublet due to phosphorus–proton coupling, since the three CH_3O-groups become equivalent on a time average owing to symmetry considerations and to conformer population[8] (for example, the environment of $CH_3'O$ in **a**, of $CH_3''O$ in **e**, and of CH_3O in **f̄** are identical and the three bipyramids **a**, **e**, **f̄** are stereochemically equivalent).

The coalescence temperature of the ^{1}H nmr signals due to the three CH_3O–groups in the 1,4,2-dioxaphospholane **14** was about −110°. The corre, sponding temperature[3–5] for the 1,2-oxaphospholene-4-**16**, was *ca.* −40°.

Evidently, the barriers for the pseudorotations in the former, **14**, were lower than those in the latter, **16** (*cf.* **16a** ⇄ **16j̄**). The differences are due primarily to differences in ring strain and in intramolecular nonbonded interactions.



16a **16j̄**

Experimental Section

The analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

***cis*- and *trans*-3,5-Di(pentafluorophenyl)-2,2,2-trimethoxy-2,2-dihydro-1,4,2-dioxaphospholanes (14 and 15).**—(1) A solution of trimethyl phosphite (5.0 g) in pentane (10 ml) was added over a 2-hr period to a suspension of pentafluorobenzaldehyde (15.8 g, 2 mol equiv) in pentane (20 ml) at 0°. The clear solution was stirred for another 2 hr at 0° and was then seeded with crystals of the pure *cis*-oxyphosphorane **14** (*vide infra*). The crystals (7.6 g, 37% yield) that separated after 15 hr at −20° had mp 79–84° and consisted of a mixture of *cis*- and *trans*-oxyphosphoranes **14** and **15** in the proportion of 95:5, as shown by ^{1}H and ^{31}P nmr spectra (see Table I). The *pure cis-oxyphosphorane* **14** was obtained after two recrystallizations from pentane–benzene (2.0 + 0.3 ml, and 4.0 + 0.4 ml per g of **14**, at −20°). This sample of **14** had mp 83–86° and was used for the variable-temperature ^{1}H nmr spectra.

Anal. Calcd for $C_{17}H_{11}O_5F_{10}P$: C, 39.5; H, 2.1; P, 6.0. Found: C, 39.3; H, 2.1; P, 5.7.

A similar analysis was obtained from mixtures of *cis*-**14** and *trans*-**15** isomers.

The mother liquid, from which the initial crop of crystals had separated, was analyzed by ^{1}H and ^{31}P nmr spectrometry in $CDCl_3$ solution. This material contained mainly **14** and **15**. It was estimated that *cis*-**14** and *trans*-**15** were originally formed in the proportion of 55:45, respectively, in about 85% of the theory. The material balance consisted of a 1,3,2-dioxaphospholane[11] isomer ($\delta^{31}P$ +50.2 ppm in $CDCl_3$), and of small amounts of substances with ^{31}P nmr signals at −0.9 (phosphate), −2.2 [$(CH_3O)PO$], −17.1, and −32.6 ppm.

(2) To obtain seeds of *cis*-oxyphosphorane **14**, the original pentane solution was kept for 5 days at −20°. The *cis–trans* mixture (50% yield) was recrystallized twice from pentane to give **14**.

(3) The relative amounts of by-products which accompanied the oxyphosphoranes **14** and **15**, increased somewhat when the original pentane solution was kept for 4 hr at 0° and for *10 hr at 25°* prior to removal of solvent at 25° (20 mm). The resulting material [20.6 g from 5 g of $(CH_3O)_3P$ and 15.8 g of C_6F_5COH] was crystallized from pentane (15 ml, 5 days, at −70° and at −20°). The crystalline *cis*-**14** and *trans*-**15** mixture (10.5 g, 90:10 proportion) had mp 83–86°. The pentane filtrate was evaporated and the residue was analyzed by ^{31}P nmr in $CDCl_3$ solution. The shifts and their approximate relative proportions were +50.2 (1.0, 1,3,2-dioxaphospholane),[11] +38.5 (6.0, *trans*-**15**), +34.3 (3.6, *cis*-**14**), −0.9 and −2.2 (3.2 combined), −17.1 (1.3), and −32.6 (1.7).

(4) The reaction of the phosphite with the aldehyde was also carried out in CH_2Cl_2 at 0°. The results were similar to those in pentane, but the relative amounts of by-products increased somewhat.

Low-Temperature Nmr Spectra.—The *cis*-oxyphosphorane **14** (*ca.* 50 mg) was placed in a thick-walled nmr tube cooled at −78°; the tube was $^3/_4$ filled with "Freon 12" (CF_2Cl_2, bp −28°, mp −155°). The tube was immersed in liquid N_2, evacuated to 10^{-6} mm, sealed, and then allowed to reach 20° slowly and with protection against possible rupture. The solutions did not show changes within 2 weeks. The results are given in Figure 1. The temperatures are regarded as accurate within 5°, by calibration with CH_3OH and by comparisons among spectra in the Varian A-60 and HA-100D at equal temperatures down to −100°. Extrapolation was used to estimate temperatures between −100 and −145°. In CF_2Cl_2 at −140° the signals were at: τ 3.56 (J_{HP} = 1.0 cps, C-5H), 4.75 (J_{HP} = 17.7 cps, C-3H), 6.28 (J_{HP} = 12.4 cps), and 6.31 (J_{HP} = 12.9 cps) for the *equatorial* CH_3O *groups*, and 6.48 (J_{HP} = 10.8 cps) for the *apical* CH_3O *group*. The spectra were also examined in $CDCl_3$ from 30 to −70°.

Registry No.—**14,** 21309-22-8; **15,** 21309-23-9.

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Allylic Sulfenyl Chlorides. A New Synthesis of Substituted 1,4-Dithianes

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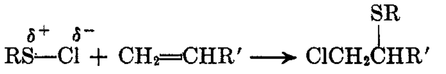
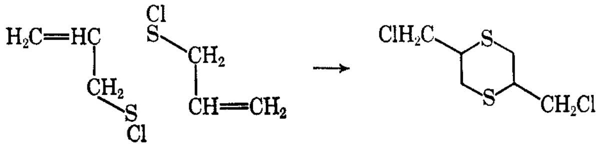
Allylsulfenyl chloride and methallylsulfenyl chloride are proposed as reactive intermediates formed from the chlorination of the corresponding disulfides. Subsequent reactions of these intermediates produce 2,5-bis-(chloromethyl)-1,4-dithianes in good yield.

Simple aliphatic sulfenyl chlorides react with terminal olefins to preferentially produce β-chloro thio ethers with chlorine on the terminal carbon (*anti*-Markovnikov addition, eq 1).[2] This preferred direction of addition



$$\overset{\delta+}{RS}\text{—}\overset{\delta-}{Cl} + CH_2\text{=}CHR' \longrightarrow ClCH_2\overset{SR}{\overset{|}{C}}HR' \qquad (1)$$

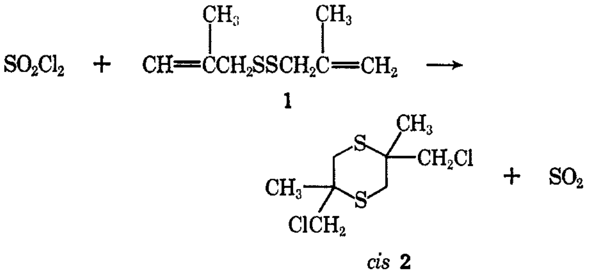
generally occurs in the absence of certain special substituents which reverse the direction of episulfonium ion ring opening and tend to favor Markovnikov addition.[3] Allylic sulfenyl halides are unusual in the sense that they contain both a sulfenyl chloride group and a reactive olefin site in the same molecule, and as such could exist only as transient reaction intermediates. However, both the sulfenyl chloride and olefinic portions of such a molecule are analogous to the simple sulfenyl chloride–olefin system and should behave in the expected manner. Under the proper conditions, therefore, reaction of allylic sulfenyl halides should produce cyclic dithiane derivatives (eq 2).



(2)

Results and Discussion

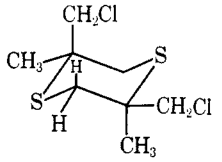
Chlorination of dilute solutions of allylic disulfides provides a convenient synthesis of 1,4-dithiane containing $ClCH_2$– groups in the 2 and 5 positions of the ring. The reaction of methallyl disulfide (**1**) with sulfuryl chloride produced a dimer or methallylsulfenyl chloride in good yield (eq 3) along with a minor amount of oligomer. Elemental analysis and molecular weight determination were consistent with the molecular formula $C_8H_{14}S_2Cl_2$. Because of a difference in solubility in chloroform, enriched fractions of the 2,5-bis(chloromethyl)-2,5-dimethyl-1,4-dithiane (**2** and **3**) isomers could be obtained and identified by nmr analysis.



(3)

cis **2**
trans **3**

The nmr spectra of **2** and **3** have peaks (in a 2:2:3 ratio) characteristic for isolated methylene groups next to both sulfur and chlorine and for a tertiary methyl group adjacent to sulfur.[4] The axial and equatorial protons of the ring methylene groups are chemically shifted (see Figure 1) owing to their different magnetic environments and appear as a pair of AB doublets. The methylene protons next to chlorine are likewise nonequivalent owing to their proximity to the asymmetric center and also comprise an AB system. The isolated tertiary methyl groups are three-proton singlets as expected. Taken together with the physical and chemical evidence, the nmr data provide convincing evidence for the isomeric dithiane structures for **2** and **3** (Table I).



2

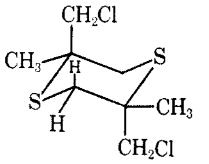


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TABLE I

NMR DATA FOR 2 AND 3[a]

Compd	Protons	Chemical shift, δ (ppm)	Designation (Figure 2)	Multiplicity (*J*, cps)
2	CH_3	1.46 (3H)		s
	CH_2S	2.97 (1 H)	H_e	d (J_g = 14.5)
		2.80 (1 H)	H_f	d
	CH_2Cl	3.56 (1 H)	H_h	d (J_g = 10.8)
		3.98 (1 H)	H_g	d
3	CH_3	1.31 (3 H)		s
	CH_2S	ax 2.97 (1 H)	H_e	dd (J_g = 14.5, ^4J = 1.3)
		eq 2.80 (1 H)	H_d	d
	CH_2Cl	n 3.58 (1 H)	H_a	d (J_g = 10.6)
		x 4.46 (1 H)	H_b	dd

[a] s, singlet; d, doublet; t, triplet; n, *endo;* x, *exo;* ax, axial; eq, equatorial.

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[1] To whom inquiries should be directed.

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[3] W. A. Thaler, W. H. Mueller, and P. E. Butler, *ibid.*, **90,** 2069 (1968).

[4] P. E. Butler, W. H. Mueller, and J. J. R. Reed, *Environ. Sci. Tech.*, **1,** 315 (1967).