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A Test for Pseudorotation in "Pentacoordinate" Sulfur Compounds¹

Sir:

That base-catalyzed hydrolysis of *cis*- and *trans*-1-ethoxy-1-phenyl-2,2,3,4,4-pentamethylphosphetanium hexachloroantimonates (1) proceeds with P-O cleavage and essentially complete retention of configuration,² whereas analogous acyclic ethoxyphosphonium salts undergo inversion of configuration under the same reaction conditions,³ has been attributed⁴ to pseudorotation in the intermediate cyclic phosphoranes. We wish to report our observation that *cis*- and *trans*-1-ethoxy-3-methylthietanium hexachloroantimonates (2) undergo base-catalyzed hydrolysis with essentially complete inversion of configuration, as do the acyclic, five- and six-membered ring analogs,⁵ and that the contrast in behavior between the phosphorus (1) and sulfur (2) systems may be taken as evidence against pseudorotation in "pentacoordinate" sulfur intermediates.⁶

Oxidation⁸ of 3-methylthietane⁹ gave a mixture of *cis*- and *trans*-3-methylthietane 1-oxides (3) which were separated by chromatography on silica gel. The isomers, 3A and 3B, respectively identified as *cis* and *trans* by their characteristic¹⁰ nmr absorption in the methylene

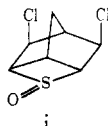
(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

(2) K. E. DeBruin, G. Zon, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, in press.

(3) G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *ibid.*, in press; R. A. Lewis, K. Naumann, K. E. DeBruin, and K. Mislow, *Chem. Commun.*, in press.

(4) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, in press.

(5) (a) C. R. Johnson and D. McCants, Jr., *ibid.*, 87, 5404 (1965); H. Hogeveen, G. Maccagnani, and F. Montanari, *J. Chem. Soc., C*, 1585 (1966). (b) It has been shown by F. Lautenschlaeger, *J. Org. Chem.*, 31, 1679 (1966), that sulfoxide i is converted to the epimer by O-ethylation, followed by base-catalyzed hydrolysis.



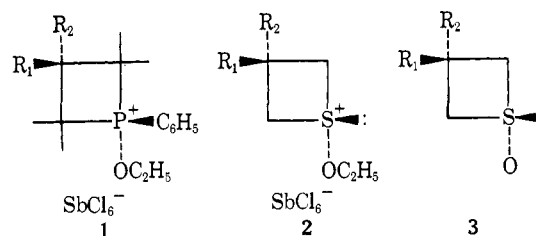
(6) Reference is made to tetracoordinate sulfur compounds of the type :SR₄, and the term "pentacoordinate" is thus a misnomer. However, deliberate use of this term is nevertheless justified as a reminder of the presence of the lone pair, a phantom ligand, and to emphasize the distinction between :SR₄ and other compounds in which sulfur also exhibits a coordination number of four, e.g., sulfones. Ligand definition thus includes a nonbonding electron pair residing in a valence orbital.⁷

(7) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), 20, 245 (1966).

(8) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, 27, 282 (1962).

(9) F. G. Bordwell and W. A. Hewett, *ibid.*, 23, 636 (1958).

(10) C. R. Johnson and W. O. Siegl, *Tetrahedron Lett.*, 1879 (1969).



A, R₁ = H; R₂ = CH₃

B, R₁ = CH₃; R₂ = H

region, had the following nmr signals: 3A, CH₃, d, τ 8.75; CH₂, m, τ 7.35–6.85 and 6.50–6.00; CH, m, τ ca. 7.60; 3B, CH₃, m, τ 8.72; CH₂, m, τ 6.70; CH, m, τ ca. 6.78. Since 3B has no measurable signal downfield of τ 6.50, and since the downfield half of the methylene multiplet due to 3A is unencumbered by interfering signals, integration of that portion of the multiplet (corresponding to two out of the total of five ring protons in 3A) provides a convenient measure of the 3A content of the mixture. A mixture consisting of 99% of 3A and 1% of 3B was O-ethylated with triethyloxonium hexachloroantimonate in dichloromethane. Base-catalyzed hydrolysis of the resulting salt (2) with 0.5 M NaOH in 50% (v/v) aqueous dioxane at room temperature afforded a mixture consisting of ca. 7% of 3A and ca. 93% of 3B. Ethylation of this mixture, followed by base-catalyzed hydrolysis of 2, as described above, led to a mixture consisting of 94% of 3A and 6% of 3B. These experiments proved that hydroxide displaces ethoxide in 2 with ≥95% inversion of configuration at sulfur.

If the reaction proceeds by a direct S_N2 displacement at sulfur, with the O-S-O angle near 180°, considerable angle strain is introduced by the presence of a four-membered ring. The equatorial (e) positions in the transition state, normally near 120° in the unstrained cases, are now forced to subtend an angle near 90°. However, if we assume the intermediacy of a "pentacoordinate" sulfur compound^{7,11} (hemisulfoxal¹² 4) of approximately trigonal-bipyramidal geometry,^{7,13} the thietane ring comfortably spans the 90° angle subtended by the apical (a) and e positions. Starting from *cis*-2 (2A), and disregarding isomers in which the thietane ring spans other than ae positions, three diastereomers of 4 (A-C), and their enantiomers, may be formed. Of these, 4C represents a high-energy form since both electronegative groups occupy the unfavorable^{13,14} e positions while the lone pair, whose position in SF₄ is equatorial,^{7,13} now occupies the a position. If 4A is first formed, only pseudorotation¹⁵ (one step) to 4B

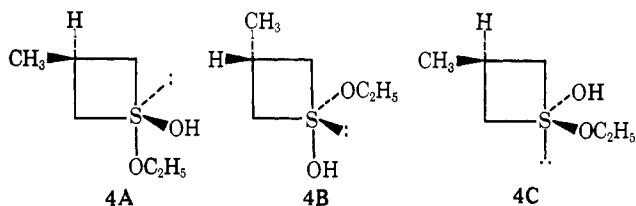
(11) Aryl and perfluoroalkyl derivatives of SF₄ have been isolated and characterized: W. A. Sheppard, *J. Amer. Chem. Soc.*, 84, 3058 (1962); R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, 1, 756 (1962). "Pentacoordinate" sulfur compounds have been invoked as intermediates in organic reactions with less electronegative groups than fluorine as ligands: B. M. Trost, R. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, 91, 2175 (1969), and references cited therein; cf. also J. Jacobus and K. Mislow, *ibid.*, 89, 5228 (1967); W. A. Pryor and U. Tonellato, *ibid.*, 89, 3379 (1967); G. H. Wiegand and W. E. McEwen, *J. Org. Chem.*, 33, 2671 (1968).

(12) The term "sulfoxal" was coined by N. J. Leonard and C. R. Johnson, *J. Amer. Chem. Soc.*, 84, 3701 (1962), to describe "pentacoordinate" sulfur compounds of the structure R₂S(OR)₂.

(13) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 3, 1298 (1964).

(14) P. C. Van der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, 88, 3255 (1966).

(15) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968), and references cited therein.



leads to a structure which is not ruled out on energetic grounds.¹⁶ Similarly, if **4B** is first formed, only **4A** is accessible¹⁶ by pseudorotation. It follows that if the rate of departure of the leaving group is faster than pseudorotation to an unfavorable intermediate,¹⁶ loss of ethoxide from **4A** or **4B** results in net retention of configuration.^{17,18} Since this is not what is observed, we conclude that the displacement at sulfur occurs by way of a high-energy transition state or intermediate: either the thietane ring spans the ee positions (I strain) and the entering (hydroxide) and leaving (ethoxide) groups occupy a positions, or the ring spans the ae positions but the entering and leaving groups now occupy e positions, with the lone pair in the a position (stereoelectronic strain). Hence, either pseudorotation in the family of "pentacoordinate" sulfur compounds, if it occurs at all,^{18,19} is less facile than in the phosphoranes, or the reaction does not proceed through an intermediate of significant lifetime and is better described as a direct nucleophilic substitution.²⁰

(16) Intermediates ruled out are those in which the thietane ring spans other than ae positions, and those in which the unfavorable energetics detailed for **4C** obtain.

(17) The principle of microscopic reversibility,¹⁵ as applied to the present case, obtains for equatorial attack (**3A** → **2A** → **4A** → **4B** → **3A**) or apical attack (**3A** → **2A** → **4B** → **4A** → **3A**).

(18) Arguments entirely analogous to the above apply to the *trans* series of **2** and **3**.

(19) E. L. Muetterties and W. D. Phillips, *J. Chem. Phys.*, **46**, 2861 (1967).

(20) NOTE ADDED IN PROOF. The present analysis is applicable *in toto* to nucleophilic substitution at phosphorus in 1-chloro-2,2,3,4,4-pentamethylphosphetane, which is also reported to proceed with inversion of configuration (D. J. H. Smith and S. Trippett, *Chem. Commun.*, 855 (1969)).

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Stereomutation of Phosphine Oxides by Lithium Aluminum Hydride¹

Sir:

Phosphine **1**, prepared by lithium aluminum hydride (LAH) reduction of optically active **2**, provided the first example of a compound whose optical activity could be attributed to stably pyramidal trivalent phosphorus.² Surprisingly, however, reduction of optically active **3** with LAH gave racemic **4**,³ even though phosphines are configurationally stable at temperatures employed in the reduction.^{2,4} We now report our finding that phos-

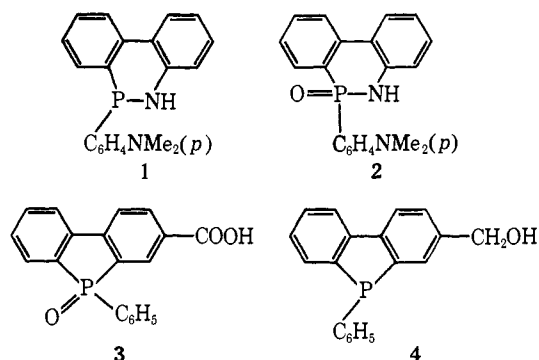
(1) We are grateful to the Air Force Office of Scientific Research for support of this research under Grant No. AF-AFOSR-1188-B, and to the Public Health Service for a Special Research Fellowship (P. D. H.).

(2) I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 5034 (1960).

(3) I. G. M. Campbell and J. K. Way, *ibid.*, 2133 (1961).

(4) L. Horner and H. Winkler, *Tetrahedron Lett.*, 461 (1964); L. D. Quin, J. P. Gratz, and R. E. Montgomery, *ibid.*, 2187 (1965); H. E. Shook, Jr., and L. D. Quin, *J. Amer. Chem. Soc.*, **89**, 1841 (1967); S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Lett.*, 5799 (1968); K. L. Marsi, *Chem. Commun.*, 846 (1968); *J. Amer. Chem. Soc.*, **91**, 4724 (1969).

phine oxides undergo rapid stereomutation in the presence of LAH *prior* to reduction.



Solutions of (+)-methylphenyl-*n*-propylphosphine oxide (**5**, 1 mmol) and LAH (0.5 mmol) in tetrahydrofuran (THF) were allowed to stand at room temperature, and their compositions were examined at hourly intervals. The results for two runs are collected in Table I

Table I. Racemization and Reduction of (+)-Methylphenyl-*n*-propylphosphine Oxide (**5**) by Lithium Aluminum Hydride in Tetrahydrofuran

Reaction time, hr	Recovered phosphine oxide ^a				Yield of phosphine, % ^b
	Run no. 1 [α] _D , deg	Run no. 1 Racemization, %	Run no. 2 [α] _D , deg	Run no. 2 Racemization, %	
0	9.8	0	18.0	0	0
1	8.1	17	15.3	15	1
2	7.5	23			2
3	4.9	50	9.8	46	5
4	4.5	54	6.8	62	7
5	3.2	67	6.4	64	9
6	1.7	83	3.6	80	9

^a Rotations of **5** refer to methanol. Starting materials are 49% (run 1) and 90% (run 2) optically pure, based on the absolute rotation of [α]_D 20°: J. P. Casey, R. A. Lewis, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2789 (1969). Recovery of **5** was generally about 70%. ^b These figures, assessed by glpc (2 ft, 10% SE-30 on 60–80 Chromosorb W), are approximate, and refer to both runs. In addition to phosphines, some other unidentified decomposition products were also observed.

and clearly demonstrate that *racemization of the phosphine oxide is virtually complete before more than 10% has been reduced to phosphine*. A control experiment showed that quenching of the reduction mixture with H₂¹⁸O does not lead to incorporation of ¹⁸O into the recovered phosphine oxide. Exposure of optically active **5** to LAH in refluxing THF or di-*n*-butyl ether at 80–90° for 30 min leads to racemic **5**. Sodium borohydride in ethanol at room temperature is ineffective as either a racemizing or reducing agent.

Exposure of either *cis*- or *trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxide⁵ to LAH in THF at room temperature produces the *same* mixture of isomers (70% recovery) consisting of 95% of the higher melting (presumably *cis*⁶) and 5% of the lower melting (presumably *trans*⁶) isomer. Significantly, the epimerization of the two diastereomers is complete within 10 min or less under the stated reaction conditions.

(5) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967).

(6) These assignments are tentative (ref 5; S. E. Cremer, private communication).