

rivative<sup>11</sup> and which has been inferred for the cobalt complex **2**.<sup>3</sup>

**Acknowledgment.** We are grateful to Professor E. Grunwald for helpful discussions and to Mr. T. Marks of the Massachusetts Institute of Technology for assistance in carrying out the computation. This work was supported by a grant from the National Science Foundation (GP-8714), which is gratefully acknowledged.

- (11) F. A. Cotton and C. R. Reich, *J. Am. Chem. Soc.*, **91**, 847 (1969).  
 (12) NDEA Title IV Fellow.

D. Ciappenelli,<sup>12</sup> M. Rosenblum

Department of Chemistry, Brandeis University  
 Waltham, Massachusetts 02154

Received July 23, 1969

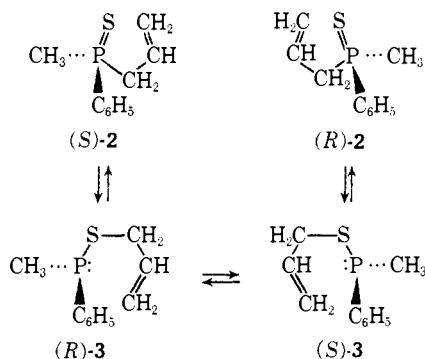
### Stereomutation of a Tetracoordinate Phosphorus Compound by Intramolecular Ligand Exchange<sup>1</sup>

Sir:

It has been established that the thermal racemization of allyl sulfoxides proceeds by a concerted, reversible, and intramolecular rearrangement mechanism.<sup>2</sup> We now wish to report the first example of an analogous process in which phosphorus is the chiral center.

Hexachlorodisilane reduction<sup>3</sup> of (+)-(*R*)-allylmethylphenylphosphine oxide (**1**),<sup>4</sup> followed by treatment of the resulting phosphine with elemental sulfur, gave (-)-(*S*)-allylmethylphenylphosphine sulfide (**2**),<sup>5</sup> which was found to racemize in *o*-xylene with first-order kinetics:  $k_{\text{rac}} \times 10^6$  (sec<sup>-1</sup>) = 3.53 (at 205°), 8.92 (at 215°), 10.4 (at 221°), and 14.7 (at 225°), whence  $E_a = 33 \pm 2$  kcal/mol and  $\log A = 9.6$  ( $\Delta S^\ddagger - 18$  eu).

#### Scheme I



According to the racemization route depicted in Scheme I, (*S*)-**2** undergoes a [2,3] sigmatropic rearrangement<sup>6</sup> to allyl (*R*)-methylphenylthiophosphinite (**3**), which is converted to (*S*)-**3** by pyramidal inversion at phosphorus. Allylic rearrangement of (*S*)-**3** to (*R*)-**2** completes the conversion of (*S*)-**2** into its enantiomer.<sup>7</sup>

(1) We are grateful to the Air Force Office of Scientific Research for support of this research under Grant No. AF-AFOSR-1188-B.

(2) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3138 (1966); K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967); P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4869 (1968).

(3) K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 2788 (1969).

(4) A. W. Herriott and K. Mislow, *Tetrahedron Lett.*, 3013 (1968).

(5) Experimental details of this preparation are reported elsewhere (G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, in press).

(6) A. Jefferson and F. Scheinmann, *Quart. Rev.* (London), **22**, 391 (1968).

(7) It is not known which of the two steps is rate determining.

The rearrangement step is reversible: allyl diphenylthiophosphinite rearranges to allyldiphenylphosphine sulfide.<sup>8</sup> That the rearrangement is concerted was demonstrated by the observation that crotyl diphenylthiophosphinite and  $\alpha$ -methylallyl diphenylthiophosphinite readily and completely (>95%) rearrange to  $\alpha$ -methylallyldiphenylphosphine sulfide and crotyldiphenylphosphine sulfide, respectively.<sup>9</sup> The rearrangement of racemic **3**<sup>10</sup> in 1,2-C<sub>6</sub>H<sub>4</sub>(CD<sub>3</sub>)<sub>2</sub> is also complete (>99%) and follows first-order kinetics:<sup>11</sup>  $k \times 10^4$  (sec<sup>-1</sup>) = 0.48 (at 21°), 1.27 (at 30°), and 5.18 (at 42°), whence  $E_a = 20$  kcal/mol and  $\log A = 10.8$  ( $\Delta S^\ddagger - 11$  eu). The negative entropy of activation attests to the cyclic character of the transition state in the rearrangement of **3** to **2**. It is interesting to note that the rearrangement of allyl thiophosphinites such as **3** is considerably more facile than that of the analogous allyl phosphinites.<sup>4</sup>

The proposed mechanism for racemization of **2** is completely analogous to that of the racemization of allyl sulfoxides,<sup>2</sup> the chief difference residing in the nature of the conformational interconversions which take place at the intermediate stage; whereas both torsion and pyramidal inversion are required to interconvert enantiomeric thiophosphinites,<sup>12</sup> torsion alone (about single bonds) suffices to interconvert enantiomeric conformers of sulfenates. Racemization in either system may thus be viewed as an intramolecular ligand exchange which proceeds in two discrete steps: a rearrangement step, in which bonds are made and broken in a concerted [2,3] sigmatropic process, and the racemization step proper, a conformational change in which bonds are neither made nor broken.

Extensions of the processes herein described to those in isoelectronic phosphorus-containing systems are readily envisaged.<sup>15</sup>

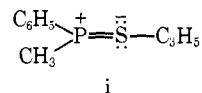
(8) A. E. Arbuzov and K. V. Nikonorov, *Zh. Obshch. Khim.*, **18**, 2008 (1948).

(9) The diphenylthiophosphinites were prepared from crotyl and  $\alpha$ -methylallyl thiol by the procedure of Arbuzov and Nikonorov.<sup>8</sup> The sulfides from each rearrangement were >95% homogeneous by pmr (CDCl<sub>3</sub>), as gauged by the well-separated and characteristic methyl proton resonances. In crotyldiphenylphosphine sulfide these appear at  $\tau$  8.26–8.52 (m), whereas in the  $\alpha$ -methylallyl isomer the A portion of an A<sub>3</sub>BX spin system is centered at  $\tau$  8.76, with  $J_{\text{HCH}} = 7$  Hz and  $J_{\text{HCP}} = 18$  Hz.

(10) Prepared from methylphenylbromophosphine and the lithium salt of allyl thiol.

(11) As measured by the rate of attenuation of the methyl doublet ( $\tau$  8.63,  $J_{\text{HCP}} = 7.5$  Hz) of **3** and the rate of growth of the methyl doublet ( $\tau$  8.51,  $J_{\text{HCP}} = 13$  Hz) of **2**.

(12) Pyramidal flattening may be facilitated by  $p\pi-d\pi$  overlap of the lone pair of electrons on phosphorus with the 3d orbital of sulfur (see i). Similar effects have been proposed to rationalize facilitated pyramidal inversion in diphosphines<sup>13</sup> and thiol sulfenates.<sup>14</sup> The same factor may also contribute to the ease of racemization of **2**, relative to the corresponding phosphine oxide, **1**.<sup>4</sup>



(13) J. B. Lambert and D. C. Mueller, *J. Amer. Chem. Soc.*, **88**, 3669 (1966).

(14) P. Koch and A. Fava, *ibid.*, **90**, 3867 (1968).

(15) For example, the racemization of allylic sulfoxides<sup>2</sup> has been discussed in its relation to the rearrangement of sulfonium ylids (J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 538 (1968)).

(16) (a) National Science Foundation Trainee, 1968–1969; (b) National Science Foundation Postdoctoral Fellow, 1967–1968.

William B. Farnham,<sup>16a</sup> Arthur W. Herriott,<sup>16b</sup> Kurt Mislow

Department of Chemistry, Princeton University  
 Princeton, New Jersey 08540

Received August 21, 1969