

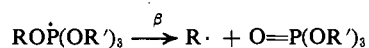
# Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XII. Self-Reactions of Some Phosphorus Centered Radicals<sup>1</sup>

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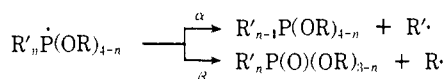
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada. Received July 12, 1973

**Abstract:** The rates of the bimolecular self-reactions of a variety of phosphorus centered radicals have been studied by kinetic epr spectroscopy. In the absence of steric effects, planar phosphinyl radicals, *e.g.*, (EtO)<sub>2</sub>P<sup>•</sup>, tetrahedral phosphonyl radicals, *e.g.*, (EtO)<sub>2</sub>P=O, and trigonal bipyramidal phosphoranyl, *e.g.*, *t*-BuOP(OEt)<sub>2</sub>Cl, and spiroposphoranyl, *e.g.*,  $\overline{\text{OCH}_2\text{CH}_2\text{O}}\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{O}$ , radicals react at (or close to) the diffusion-controlled limit.

Over the past 4 years epr spectroscopy has been extensively used in the study of phosphorus centered radicals in solution.<sup>4-14</sup> The epr spectra have their own intrinsic interest and provide a method of measuring radical concentrations and hence a method for following the kinetic behavior of the radicals. The unimolecular reactions of phosphorus centered radicals have received the most attention. Thus, the kinetics for  $\beta$ -scission of some tetraalkoxyphosphoranyl rad-



icals have been measured by monitoring phosphoranyl decay directly<sup>11</sup> and by a "steady-state" technique<sup>5,11</sup> in which the concentrations of photolytically generated radicals were measured as a function of light intensity. Similar techniques have been applied to elucidate the factors controlling the relative importance of  $\alpha$ - and  $\beta$ -scission processes in alkyl alkoxy phosphoranyls,<sup>6</sup> a problem that has also been tackled by conventional product studies.<sup>15</sup>



Kinetic and rate data for the bimolecular self-reactions of only two phosphorus centered radicals have

- (1) Issued as National Research Council of Canada No. 10000. Part XI: V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6400 (1973).
- (2) National Research Council of Canada Postdoctorate Fellow, 1972-1973.
- (3) Department of Chemistry, University College, London, England.
- (4) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969).
- (5) (a) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, **10**, 738 (1970); (b) *J. Amer. Chem. Soc.*, **94**, 1782 (1972); (c) *J. Chem. Soc., Perkin Trans. 2*, 993 (1972); (d) *ibid.*, 2224 (1972).
- (6) A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **40**, C33 (1972).
- (7) (a) D. Griller and B. P. Roberts, *J. Organometal. Chem.*, **42**, C47 (1972); (b) *J. Chem. Soc., Perkin Trans. 2*, 1416 (1973).
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- (9) G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 2528 (1972).
- (10) P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6033 (1972).
- (11) G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 8784 (1972).
- (12) K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 420 (1973).
- (13) P. J. Krusic and P. Meakin, *Chem. Phys. Lett.*, **18**, 347 (1973).
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- (15) (a) W. G. Ben-trude, E. R. Hansen, W. A. Khan, T. B. Min, and P. E. Rogers, *J. Amer. Chem. Soc.*, **95**, 2286 (1973); (b) W. G. Ben-trude, J. J. L. Fu, and P. E. Rogers, *ibid.*, **95**, 3625 (1973), and references cited.

been reported, *viz.*, *t*-BuOP(OEt)<sub>3</sub> and *t*-BuOP(OEt)<sub>3</sub>.<sup>11</sup> In the present paper we report similar data for a number of phosphorus centered radicals that have been chosen to cover a wide variety of structures.

Esr spectral parameters for the first phosphinyl radicals detected in solution, (EtO)<sub>2</sub>P<sup>•</sup> and (Me<sub>2</sub>N)<sub>2</sub>P<sup>•</sup>, are also reported.

## Experimental Section

The general experimental techniques and kinetic procedures have been adequately described in previous papers in this series.<sup>1</sup> The kinetics of the decay of the phosphorus centered radicals were studied at radical concentrations in the range 10<sup>-6</sup>-10<sup>-7</sup> M.

**Materials.** Most of the phosphorus compounds used in this work were either commercially available or were synthesized as previously described.<sup>7</sup>

**Tetrakis(dimethylamino)diphosphine** was prepared by the method of Nöth and Vetter.<sup>16</sup>

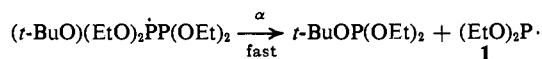
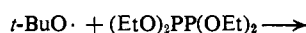
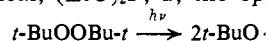
**Tetraethoxydiphosphine** was prepared under nitrogen in very low yield by refluxing diethyl chlorophosphite (7 g) with sodium (2 g) in isoctane (70 ml) with stirring for 30 min. Fractional distillation at reduced pressure gave 0.2 g (3.7%) of product: bp 60° (0.1 Torr); nmr <sup>1</sup>H chemical shifts (in ppm from TMS) 1.20 (CH<sub>3</sub>, J<sub>H-H</sub> = 7.1 Hz) and 3.9 (CH<sub>2</sub>, J<sub>POCH</sub> = 8.3 Hz).

**Tetramethyldiphosphine<sup>17</sup>** and **tetra-tert-butylidiphosphine<sup>18</sup>** were prepared by standard methods.

## Results

### Reaction of *tert*-Butoxy Radicals with Diphosphines.

Photolysis in the epr cavity of a solution of di-*tert*-butyl peroxide containing tetraethoxydiphosphine gave a simple doublet spectrum attributed to the diethoxyphosphinyl radical, (EtO)<sub>2</sub>P<sup>•</sup>, **1**, the epr parameters for



which are:  $a(^3\text{P}) = 78.5$  G,  $g = 2.0018$ , no resolvable fine structure. The presumed phosphoranyl intermediate, (t-BuO)(EtO)<sub>2</sub>P<sup>•</sup>P(OEt)<sub>2</sub>, could not be detected even at -80° and must therefore undergo a very rapid  $\alpha$ -scission. The *tert*-butyl diethyl phosphite showed no sign of reacting with another *tert*-butoxy radical to yield the phosphoranyl (t-BuO)<sub>2</sub>P(OEt)<sub>2</sub>, presumably because the diphosphine is much more reactive and "mops-up" all the *tert*-butoxy radicals.

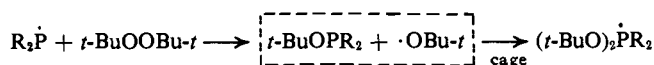
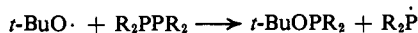
(16) H. Nöth and H. J. Vetter, *Chem. Ber.*, **94**, 1505 (1961).

(17) H. Niebergall and B. Langenfeld, *Chem. Ber.*, **95**, 64 (1962).

(18) K. Issleib and M. Hoffmann, *Chem. Ber.*, **99**, 1320 (1966).

Analogous results were obtained in a similar experiment using tetrakis(dimethylamino)diphosphine. The bis(dimethylamino)phosphinyl radical,  $(\text{Me}_2\text{N})_2\dot{\text{P}}$ , **2**, gave an epr spectrum consisting of a doublet of multiplets:  $a(^{31}\text{P}) = 70.2 \text{ G}$ ,  $a_{\text{N}} (2 \text{ N}) = 4.2 \text{ G}$ ,  $a_{\text{H}} (12 \text{ H}) = 2.1 \text{ G}$ ,  $g = 2.0032$ . The splittings were determined by computer simulation.

Quite different behavior was exhibited by tetramethyl- and tetra-*tert*-butyldiphosphine. In both cases only the spectrum of the dialkyldi-*tert*-butoxyphosphoranyl could be detected.<sup>10</sup> Possibly a dialkylphosphinyl radical is produced initially and this rapidly inserts itself into the peroxidic bond.

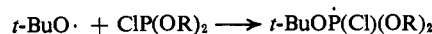
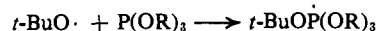


$(t\text{-BuO})_2\dot{\text{P}}\text{Me}_2$ ,  $a(^{31}\text{P}) = 701 \text{ G}$ ;  $a_{\text{H}} = 2.5 \text{ G}$ ;  $g = 2.004^{19}$  at  $-100^\circ$

$(t\text{-BuO})_2\dot{\text{P}}\text{-}t\text{-Bu}_2$ ,  $a(^{31}\text{P}) = 705 \text{ G}$ ;  $g = 2.004^{19}$  at  $-100^\circ$

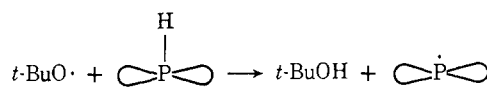
**Reactions of *tert*-Butoxy with Other Phosphorus Compounds.** The tetraalkoxyphosphoranyl radicals **3** and **4** (see Table I) and the trialkoxychlorophosphor-

phosphites,<sup>7b</sup> respectively. The epr parameters of these

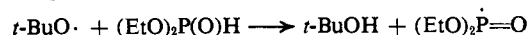


radicals have been reported previously.<sup>5a,c,7b,11</sup>

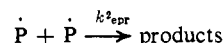
The spirophosphoranyl radicals **7–10** were obtained by hydrogen abstraction from the spirophosphoranes.<sup>7</sup>



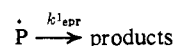
Their epr parameters have been reported.<sup>7</sup> The phosphonyl radicals **11** and **12** were obtained in the same way<sup>5b</sup>, e.g.



**Decay Kinetics.** All the phosphorus centered radicals undergo a very rapid bimolecular self-reaction at sufficiently low temperatures. For the majority of the



radicals studied this process predominates at  $-20^\circ$  and rate constants are therefore quoted at this temperature in Table I. The tetraalkoxyphosphoranyls and trialkoxychlorophosphoranyls decay, however, by a first-order process at  $-20^\circ$ . The measured (or extrapo-



lated<sup>11</sup>) first-order rate constants for these radicals are also given at  $-20^\circ$  in Table I.

The rate constants for the second-order decay of the trialkoxychlorophosphoranyls were measured at  $-90^\circ$ . We have previously measured  $k^2_{\text{epr}}$  over a temperature range from  $-120$  to  $-160^\circ$  for the two tetraalkoxyphosphoranyl radicals.<sup>11</sup> These data can be represented by eq 1 and 2. For all the other phosphorus centered

$$t\text{-BuO}\dot{\text{P}}(\text{OMe})_3, k^2_{\text{epr}} = 10^{9.3} \exp(-1750/RT) \text{ M}^{-1} \text{ sec}^{-1} \quad (1)$$

$$t\text{-BuO}\dot{\text{P}}(\text{OEt})_3, k^2_{\text{epr}} = 10^{8.8} \exp(-1700/RT) \text{ M}^{-1} \text{ sec}^{-1} \quad (2)$$

radicals the values of  $k^2_{\text{epr}}$  are sufficiently close to the diffusion-controlled limit (*ca.*  $2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ) that measurements over a range of temperature are not considered to be worthwhile. That is, any honest appraisal of the kinetic epr method indicates that the inherent experimental error in a  $k^2_{\text{epr}}$  value of  $10^8\text{--}10^9 \text{ M}^{-1} \text{ sec}^{-1}$  determined at one temperature is as great as the likely changes in its value over any readily accessible temperature range.

## Discussion

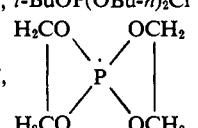
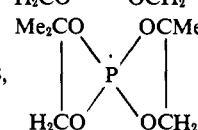
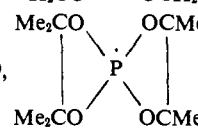
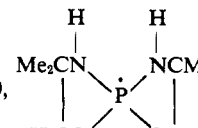
The isotropic phosphorus hyperfine splittings for our two phosphinyl radicals in solution (*viz.*, 78.5 and 70.2 G) are similar to those reported for other phosphinyls in solid matrixes, e.g., for  $\text{PF}_2$  84.6 G,<sup>20</sup> for  $\text{PCl}_2$  71 G,<sup>21</sup> and for  $\text{PH}_2$  80 G.<sup>22</sup> The relatively small magnitude of these splittings indicates that the orbital containing the unpaired electron has little or no s character. The structure proposed<sup>20</sup> for phosphinyls involves the two ligands and the lone pair lying in a

(20) W. Nelson, G. Jackel, and W. Gordy, *J. Chem. Phys.*, **52**, 4572 (1970); *cf.* also D. Kilcast and C. Thomson, *J. Chem. Soc., Faraday Trans. 2*, **68**, 435 (1972).

(21) G. F. Kokoszka and F. E. Brinckmann, *Chem. Commun.*, 349 (1968); *J. Amer. Chem. Soc.*, **92**, 1199 (1970).

(22) R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1747 (1966).

**Table I.** Rate Constants,  $k^2_{\text{epr}}$ , for the Bimolecular Self-Reactions of Some Phosphorus Centered Radicals

| Radical <sup>a</sup>  | $k^2_{\text{epr}} \times 10^{-7}$<br>( $\text{M}^{-1} \text{ sec}^{-1}$ ) <sup>b</sup> | $k^1_{\text{epr}} \times 10^{-2}$<br>( $\text{sec}^{-1}$ ) <sup>b</sup> |
|---|--|---|
| <b>1</b> , $(\text{EtO})_2\dot{\text{P}}$   | 280  |   |
| <b>2</b> , $(\text{Me}_2\text{N})_2\dot{\text{P}}$  | 110  |   |
| <b>3</b> , $t\text{-BuOP(OMe)}_3$   | $6.3^{c-e}$  | 47 <sup>e</sup>   |
| <b>4</b> , $t\text{-BuOP(OEt)}_3$   | $2.0^{c-e,f}$  | 66 <sup>e</sup>   |
| <b>5</b> , $t\text{-BuOP(OEt)}_2\text{Cl}$  | 21 <sup>e</sup>  | 1.3   |
| <b>6</b> , $t\text{-BuOP(OBu-}t\text{)}_2\text{Cl}$   | 19 <sup>e</sup>  | 4.8   |
| <b>7</b> ,   | 230  |   |
| <b>8</b> ,   | 50   |   |
| <b>9</b> ,   | 12   |   |
| <b>10</b> ,  | 13   |   |
| <b>11</b> , $(\text{EtO})_2\dot{\text{P}}=\text{O}$   | 330  |   |
| <b>12</b> , $(\text{Et})(\text{EtO})\dot{\text{P}}=\text{O}$                                    | 280  |   |

<sup>a</sup> Radicals generated by photolysis of *ca.* 1 M phosphorus compound in neat di-*tert*-butyl peroxide for measurements at  $-20^\circ$ . For measurements at  $-90^\circ$  this mixture was diluted with *ca.* 1.5 volumes of cyclopropane. <sup>b</sup> At  $-20^\circ$  unless otherwise noted. <sup>c</sup> Calculated from Arrhenius equations (1 and 2). <sup>d</sup> At  $-90^\circ$ ,  $k^2_{\text{epr}} = 1.6 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ . <sup>e</sup> Extrapolated from lower temperatures. See ref 11. <sup>f</sup> At  $-90^\circ$ ,  $k^2_{\text{epr}} = 5.8 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ . <sup>g</sup> At  $-90^\circ$ .

anyl radicals **5** and **6** were prepared by *tert*-butoxy addition to the appropriate phosphite<sup>5a,c,11</sup> and chloro-

(19) R. W. Dennis, unpublished results.

plane with the central phosphorus atom and the unpaired electron being contained in an almost pure *p* orbital perpendicular to this plane.

The radicals chosen for the present work include examples from most of the known major structural types of phosphorus centered radicals. Thus, the phosphinyl radicals **1** and **2** are planar, the phosphoranyl radicals **3-10** have a distorted trigonal bipyramidal structure with the unpaired electron occupying an equatorial position,<sup>5c,9,10,14,23</sup> and the phosphonyl radicals **11** and **12** are close to tetrahedral.<sup>14</sup> It is clear that in the absence of significant steric effects all three structural types react at, or close to, the bimolecular diffusion-controlled limit (*ca.*  $2 \times 10^9 M^{-1} \text{sec}^{-1}$ )<sup>24</sup> as do other simple unhindered radicals that dimerize (or disproportionate) with the release of  $\geq 20$  kcal/mol.<sup>25</sup>

Steric retardation of the reaction is only significant in the phosphoranyl radicals. It is interesting to note that **9** is more reactive than **3** or **4**. Since the bimolecular reaction almost certainly involves the formation of a P-P bonded dimer it must be concluded that steric repulsion between spirophosphoranyls is reduced rela-

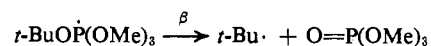
(23) These radicals may undergo "pseudorotation" in which ligands in the apical and equatorial positions in the bipyramid exchange positions. Except for **7** and **9**, these radicals may therefore exist in more than one form.<sup>5b,5b,13</sup>

(24) Dialkoxydialkylphosphoranyl radicals have remarkably long lifetimes<sup>6,10</sup> which indicates that *not all phosphoranyls* react at this rate.

(25) See, *e.g.*, G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 491 (1972); J. R. Roberts and K. U. Ingold, *ibid.*, **95**, 3228 (1973).

tive to that for analogous nonspiro radicals by appropriate orientation of the ring systems.

The tetraalkoxyphosphoranyls **3** and **4** eliminate *tert*-butyl radicals in their unimolecular decay process as is indicated by the observation of the *tert*-butyl radical under appropriate conditions,<sup>5,a,c,11</sup> *e.g.*



The trialkoxychlorophosphoranyls **5** and **6** are considerably more stable toward unimolecular decay than are the tetraalkoxyphosphoranyls, but the reason for this remains to be determined. The first-order decay process for **5** (and presumably **6**) involves the elimination of either a *tert*-butyl radical or a chlorine atom, the two processes being of approximately equal importance.<sup>15a</sup> If the radical which is eliminated reacts rapidly with a second phosphorus radical the reported first-order decay rate constants will be twice the rate constants for the actual  $\beta$ -scissions.

### Conclusion

In the absence of steric effects, phosphorus centered radicals having planar, tetrahedral, and trigonal bipyramidal geometries undergo bimolecular self-reactions at rates equal (or close) to the diffusion-controlled limit. There does not appear to be much likelihood that an unconjugated, long-lived, neutral phosphorus centered radical will be prepared.<sup>26</sup>

(26) See G. D. Mendenhall and K. U. Ingold, *Chem. Brit.*, in press.

## Mass Spectrometry in Structural and Stereochemical Problems. CCXXXIX.<sup>1</sup> Elucidation of the Ring D Cleavage in Lanostane<sup>2</sup>

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*Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received August 24, 1973*

**Abstract:** Through extensive deuterium labeling of the steroid nucleus the electron impact induced fragmentation of ring D in lanostane (and 14 $\alpha$ -methylcholestane) has been elucidated in order to provide a secure basis for the interpretation of the mass spectra of tetracyclic triterpenes. Major mechanistic differences were noted as a result of the additional methyl group at C-14. Unlike cholestane, the dominant ring D cleavage process of lanostane involves methyl loss from a partial ring D fragmentation ion; the minor cleavage process occurs with a single hydrogen transfer (the C-32 position being the main contributor). Reciprocal hydrogen transfer is a minor process. Contrary to the situation among steroids lacking a 14 $\alpha$ -methyl group this partial ring D cleavage ion is found to play a dominant role in directing all the subsequent fragmentations. The results of the deuterium labeling have made it possible to explain other important fragmentations as well. The synthesis of the analogs labeled with deuterium at positions 1, 2, 3, 6, 7, 8, 9, 11, 12, 15, 16, 18, 19, 30, 31, and 32 is described, with special emphasis on the use of the tetramethylphosphorodiamidate reduction (Ireland reaction).

The electron impact induced fragmentation of steroids possessing an alkyl side chain at C-17, such as cholestane (I) or pregnane (II), characteristically involves extensive fragmentation of ring D. In addition

to being of considerable mechanistic interest, the fragmentations are of particular diagnostic importance in determining the nature of the C-17 side chain.<sup>4</sup> Extensive deuterium labeling experiments<sup>5</sup> have revealed the precise course of these fragmentations and demon-

(1) For paper CCXXXVIII, see J. H. Block, D. H. Smith, and C. Djerassi, *J. Org. Chem.*, submitted for publication.

(2) Financial assistance from the National Institutes of Health (Grants No. GM-06840 and AM-04257) is gratefully acknowledged.

(3) National Institutes of Health Postdoctoral Fellow, 1971-1973.

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(5) L. Tokes, G. Jones, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 5465 (1968).