orders of magnitude less than the most efficient oxalate esters. However, no attempt has been made to optimize the structure of the oxazolinedione to increase light output.

Experimental Section

General Methods. Solvents were purified by distillation before use. Fluorescers were chromatographed on alumina and then recrystallized. The chemiluminescence measurements were performed by the photo-counting method at room temperature by using the apparatus previously described.[11]

Typical Chemiluminescence Measurement. A solution of oxazolinedione 1 in dimethyl phthalate was added to a solution of the fluorescer and hydrogen peroxide, also in dimethyl phthalate, so that the final volume was ca. 2.0 mL. Typical concentrations of these reagents in this solution were as follows: 1, 5.5×10^{-4} M; fluorescer, 3.5×10^{-4} M; 95% H_2O_2, 0.4 M. For the lutidine-catalyzed runs, the base was included in the peroxide solution. The light output from these solutions was monitored for ca. 4 half-lives at room temperature.

Acknowledgment. This work was supported by the Office of Naval Research.

Registry No. 1, 77903-65-2; 9,10-diphenylanthracene, 1499-10-1; hydrogen peroxide, 7722-84-1; 2,6-lutidine, 108-48-5.

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(11) Smith, J. P.; Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 1041.

Bicyclic Dioxaphosphoranes. 3.[1] Spectral Evidence for the Conformation of a Phosphorane

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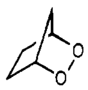
The insertion of a phosphine into the oxygen-oxygen bond of a peroxide to produce a phosphorane was first reported in 1964.[2] Since that initial report the reactions of phosphines with diacyl peroxides,[3] peresters,[4] dialkyl peroxides,[5] hydroperoxy endoperoxides,[6] ozonides,[7] and dioxetanes[8] have all been observed.

We have previously reported[1] that triarylphosphines and phosphites insert into the oxygen-oxygen bond of the prostaglandin endoperoxide model 2,3-dioxabicyclo[2.2.1]heptane (1). We presented spectral evidence that the products of these reactions were bicyclic dioxaphosphoranes which were undergoing rapid pseudorotation at room temperature. We report here the first example of the insertion of a phosphine into the peroxide linkage of 1 to produce at room temperature two noninterconverting phosphoranes kinetically isolated from each other by a high-barrier pseudorotation. The ^{13}C and ^{1}H NMR's of these phosphoranes further allow us to eliminate from consideration possible structures of these products and to estimate lower limits for the activation barriers necessary to place a bicyclo[3.2.1] structure and a four-membered ring in the equatorial-equatorial position of a trigonal bipyramid.



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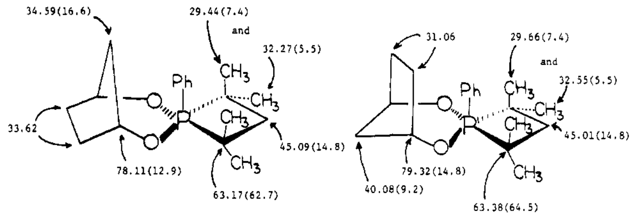
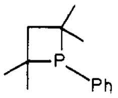


3 4

Figure 1. ^{13}C chemical shift assignments for the two phosphoranes. The carbon-phosphorus coupling constants are reported in hertz in parentheses following the chemical shift. The aromatic chemical shifts are reported in the Experimental Section.

A solution of phosphine 2[9] in dry benzene[10] was added to a serum-capped 10-mm NMR tube containing a solution of peroxide at −78 °C. Warming to room temperature resulted in the complete disappearance of 2 as indicated by the ^{31}P NMR peak at δ 49.08.[11] Concurrent with the disappearance of 2, two new peaks at δ −42.48 and −44.77 in an integrated ratio of 1.0:1.6, respectively, appeared in the ^{31}P NMR spectrum. We suggest that these two peaks are due to two structurally different and kinetically isolated phosphoranes. Consistent with this interpretation are the ^{13}C NMR spectral assignments presented in Figure 1. The ^{13}C NMR spectra are reminescent of those previously reported.[1b] Carbon-phosphorus coupling to C_5 but not $C_{7,8}$ is observed, indicative of a Karplus relationship. The assignments of the ^{13}C peaks were made with the aid of intensity measurements and the DEPT (Distortionless Enhancement of Polarization Transfer)[12] pulse sequence.



2

The NMR indicated that the yields of the two phosphoranes were essentially quantitative as revealed by the absence of any peaks attributable to starting material, byproducts, or decomposition products. (The ^{13}C NMR is available as supplementary material; see the paragraph at the end of the paper for further details.)

The observation of two different methyls by ^{13}C NMR but only one quaternary carbon in the four-membered ring of both phosphoranes precludes any conformational pro-

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(1) For parts 1 and 2 see: (a) Clennan, E. L.; Heah, Poh Choo *J. Org. Chem.* **1981**, *46*, 4105. (b) *Ibid.* **1982**, *47*, 3329.

(2) Denney, D. B.; Relles, H. M. *J. Am. Chem. Soc.* **1964**, *86*, 3897.

(3) (a) Greenbaum, M. A.; Denney, D. B.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1956**, *78*, 2563. (b) Denney, D. B.; Greenbaum, M. A. *Ibid.* **1957**, *79*, 979.

(4) Denney, D. B.; Goodyear, W. F.; Goldstein, B. *J. Am. Chem. Soc.* **1961**, *83*, 1726.

(5) Denney, D. B.; Relles, H. M. *J. Am. Chem. Soc.* **1964**, *86*, 3897.

(6) Porter, N. A.; Funk, M. O.; Gilmore, D.; Isaac, R.; Nixon, J. *J. Am. Chem. Soc.* **1976**, *98*, 6000.

(7) Carles, J.; Fliszar S. *Can. J. Chem.* **1969**, *47*, 1113.

(8) Bartlett, P. D.; Baumstark, A. L.; Landis, M. E.; Lerman, C. L. *J. Am. Chem. Soc.* **1974**, *96*, 5267.

(9) De'Ath, N. J.; Denney, D. B.; Denney, D. Z.; Hsu, Y. F. *J. Am. Chem. Soc.* **1976**, *98*, 768.

(10) The benzene was distilled from benzophenone ketyl and stirred over EDTA before use.

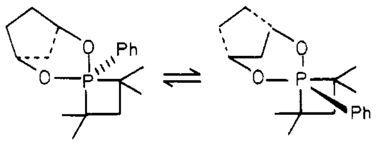
(11) All ^{31}P chemical shifts are reported relative to 85% H_3PO_4 by substitution. A negative shift is indicative of a peak appearing upfield of the reference.

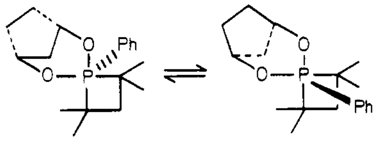
(12) (a) Bendall, M. R.; Doddrell, D. M.; Pegg, D. T. 23rd Experimental Nuclear Magnetic Resonance Conference, Madison, WI, Apr 25-29, 1982. (b) Bendall, M. R.; Pegg, D. T.; Doddrell, D. M.; Thomas, D. M. *J. Magn. Reson.* **1982**, *18*, 1.

(13) DeBruin, K. E.; Neumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7031.

0022-3263/83/1948-2621$01.50/0

cess which passes through a phosphorane in which the four-membered ring spans the equatorial–equatorial positions of the trigonal bipyramid. The ^{13}C spectral data is only consistent with the population of the trigonal bipyramids **5** and **6** or the square-pyramidal phosphoranes **3** and **4**. Heating the reaction mixture to 145 °C resulted in the slow decomposition of the phosphoranes without any indication of the onset of pseudorotation.


5 **5′**


6 **6′**

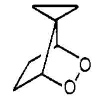
The lower limits for the activation barriers which place the four-membered and bicyclo[3.2.1] rings in the equatorial–equatorial position of a trigonal bipyramid are 19.5 kcal/mol[14] as determined by the use of eq 1 and 2.[15] The

$$k_c = \pi|\delta\nu|/2^{1/2} \qquad (1)$$

$$\Delta G^{*}{}_{T_c} = 4.57T_c(10.32 + \log T_c/k_c) \qquad (2)$$

rate constant at coalescence is determined by eq 1 where $\delta\nu$ is the difference in frequency of peaks which are averaged by the conformational process (e.g., the phenyl rings are averaged by the pseudorotation which forces the four-membered ring equatorial–equatorial and the two methyls in each phosphorane by the conformational process which forces the bicyclo[3.2.1] ring equatorial–equatorial). This represents the first estimation of the barrier necessary to place a bicyclo[3.2.1] ring equatorial–equatorial. The equatorial–equatorial four-membered ring has previously been estimated to be greater than 20 kcal/mol higher in energy than the apical–equatorial conformation,[16] consistent with our results here.

We have also examined the reaction of **2** with the tricyclic peroxide **7** and found very similar results. Two phosphoranes were formed as detected by two ^{31}P NMR peaks at −43.99 and −42.87 ppm in an integrated ratio of 1.0:1.2, respectively.


7

Experimental Section

Materials. The synthesis of bicyclic peroxides **1**[17] and **7**[18] and phosphine **2**[9] were accomplished as reported previously. All compounds gave satisfactory spectral and physical data. Benzene was distilled in a N_2 atmosphere from benzophenone ketyl and then was stirred over the disodium salt of EDTA.

Dioxaphosphoranes 3 and 4. These compounds were synthesized by addition of phosphine **2** via syringe to a serum capped 10-mm NMR tube containing **1** and benzene at −78 °C. The reaction mixture was then allowed to warm to room temperature where the spectral data were collected. ^{13}C NMR (aromatic region only) for **3** δ 127.5 (J_{P-C} = 11.1 Hz), 129.1 (J_{P-C} = 22.1 Hz), 133.3 (J_{P-C} = 9.2 Hz), and 141.7 (J_{P-C} = 97.7 Hz); for **4** δ 126.6 (J_{P-C} = 11.1 Hz), 128.4 (J_{P-C} = 16.6 Hz), 133.9 (J_{P-C} = 9.2 Hz), 139.1 (J_{P-C} = 95.9 Hz); ^{1}H NMR δ 0.7–2.2 (m, 40 H), 4.28 (d, 2 H, J_{P-H} = 15.4 Hz), 4.39 (d, 2 H, J_{P-H} = 20.5), 7.1–7.4 and 7.8–8.1 (aromatic hydrogens). The ^{1}H NMR spectra are available as supplementary materials (see the paragraph at the end of the paper for further details).

NMR Measurements. The ^{31}P NMR measurements were made on a JEOL FX270 instrument at 109.13 MHz. A total of 16 384 points were collected over a spectral width of 50 000 Hz by utilizing a pulse delay of 50 s. All the chemical shifts are reported relative to 85% H_3PO_4 by substitution. A negative chemical shift is indicative of an upfield peak. The proton and ^{13}C NMR data were also collected in benzene-d_6 on a JEOL FX270 instrument and the data referenced to tetramethylsilane by substitution.

Acknowledgment. We thank the University of Wyoming and the Biomedical Research Grant Program, Division of Research Resources, National Institutes of Health (Grant S07 BR07157), for support of this work.

Registry No. **1**, 279-35-6; **2**, 37895-59-3; **3**, 86088-70-2; **4**, 86118-04-9; **7**, 67105-55-9; 2″,2″,4″,4″-tetramethyl-3′-phenyldispiro[cyclopropane-1,8′-[2,4]dioxa[3]phosphabicyclo[3.2.1]octane-3′,1″-phosphetane] (isomer 1), 86088-71-3; 2″,2″,4″,4″-tetramethyl-3′-phenyldispiro[cyclopropane-1,8′-[2,4]dioxa[3]phosphabicyclo[3.2.1]octane-3′,1″-phosphetane] (isomer 2), 86118-05-0.

Supplementary Material Available: Full NMR data for compounds **3** and **4** (2 pages). Ordering information is given on any current masthead page.

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[14] This analysis is not dependent on the geometry of the most stable phosphorane and is correct if the phosphorane is trigonal bipyramid or square pyramidal.

[15] Peccinni-Leopardi, C.; Fabre, O.; Reisse, J. *Org. Magn. Reson.* **1976**, *8*, 233.

[16] (a) Mislow, K. *Acc. Chem. Res.* **1970**, *3*, 321. (b) Ruff, R. E.; Oram, R. K.; Trippett, S. *J. Chem. Soc., Chem. Commun.* **1971**, 1011. (c) Denney, D. Z.; White D. W.; Denney, D. B. *J. Am. Chem. Soc.* **1971**, *93*, 2066.

[17] (a) Porter, N. A.; Gilmore D. W. *J. Am. Chem. Soc.* **1977**, *99*, 3503. (b) Salomon, R. G.; Salomon, M. F. *Ibid.* **1977**, *99*, 3501. (c) Coughlin, D. J.; Brown, R. S.; Salomon, R. G. *Ibid.* **1979**, *101*, 1533.

[18] (a) Adam, W.; Erden, J. *J. Org. Chem.* **1978**, *43*, 2738. (b) Adam, W.; Eggelte, H. J. *Ibid.* **1977**, *42*, 3987.

The Solution Thermolysis of 2-, 3-, and 4-(2-Hydroxy-2-arylethyl)pyridines

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An increasing interest has recently developed in retroene reactions[1] of systems containing a carbon–nitrogen double bond and a β-hydroxy group (Scheme I). In a previous study[1] we examined compounds in which the nitrogen atom was part of a pyrazine ring. 2-(2-Hydroxy-2-arylethyl)pyrazines were found to undergo smooth retro-ene type reactions to form the corresponding aldehydes and the 2-methylpyrazines. A concerted mechanism involving a nonpolar six-membered-ring transition state was proposed for this reaction.[1]

The present investigation was aimed at extending this study to (2-hydroxyarylethyl)pyridines and, in particular, at comparing the reactivity of the 2-, 3-, and 4-pyridyl isomers of these substrates. The syntheses of these compounds were carried out by reacting the corresponding

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[1] Houminer, Y. *J. Org. Chem.* **1980**, *45*, 999 and references cited therein.

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