IR (neat) 3325 $cm^{-1}$ (OH); $^1H$ NMR ($CDCl_3$) $\delta$ 1.47 (br, OH), 2.58 (t, $J$ = 6.9 Hz, 9-$CH_2$), 3.49 (t, $J$ = 6.9 Hz, $CH_2OH$), 6.64-7.36 (m, ArH).

**9-(2-Chloroethyl)-9-phenylthioxanthene (58).** To a solution of **66** (700 mg) in benzene (10 mL) was added dropwise thionyl chloride (2 mL) and the mixture was refluxed for 1 h. Evaporation of the solvent gave an oil which soon solidified, was recrystallized from $CH_2Cl_2$-MeOH, and afforded 697 mg (94%) of **58** as colorless needles: mp 126-128 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 2.60-2.99 (m, 9-$CH_2$), 3.10-3.47 (m, $CH_2Cl$), 6.58-7.38 (m, ArH). Anal. Calcd for $C_{21}H_{17}ClS$: C, 74.87; H, 5.09. Found: C, 74.84; H, 5.00.

**9-Phenyl-9-(3-(phenylthio)propyl)thioxanthene (67).** To a solution of (3-(phenylthio)propyl)magnesium bromide prepared from 3-(phenylthio)propyl bromide[10] (6.2 g), Mg (650 mg), ether (50 mL), and catalytic amounts of $I_2$ was added **60** (4 g) in limited amounts with stirring. After refluxing for 30 min, the reaction mixture was treated with an $NH_4Cl$ solution. The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated to dryness to give an oil which was purified by column chromatography on silica gel using $CH_2Cl_2$-petroleum ether (1:4). Recrystallization of the resulting solids from hexane gave 3 g (66%) of **67** as colorless needles: mp 95-97 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.19-1.75 (m, 9-$CH_2CH_2$), 2.29-2.68 (m, 9-$CH_2$), 2.75 (t, $J$ = 6.5 Hz, $CH_2S$), 6.55-7.35 (m, ArH). Anal. Calcd for $C_{28}H_{24}S_2$: C, 79.20; H, 5.70. Found: C, 79.27; H, 5.69.

**9-(3-Iodopropyl)-9-phenylthioxanthene (59).** A mixture of **67** (1.4 g), sodium iodide (1.5 g), methyl iodide (5 mL), and DMF (10 mL) was refluxed for 24 h. The reaction mixture was poured into cold water and extracted with ether. The extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The residue was recrystallized from hexane to afford 1.27 g (87%) of **59** as colorless prisms: mp 111-113 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.35-1.88 (m, 9-$CH_2CH_2$), 2.22-2.60 (m, 9-$CH_2$), 2.98 (t, $J$ = 6.4 Hz, $CH_2I$), 6.50-7.37 (m, ArH). Anal. Calcd for $C_{22}H_{19}IS$: C, 59.73; H, 4.33. Found: C, 59.89; H, 4.32.

**X-ray Analysis of 1′.** Crystal data: $C_{20}H_{17}BF_4S$, FW = 376.22, orthorhombic, $P2_12_12_1$, $a$ = 9.976 (7) Å, $b$ = 12.099 (5) Å, $c$ = 14.700 (8) Å, $U$ = 1774.2 Å$^3$, $Z$ = 4, $D_x$ = 1.41 g/cm$^3$, $\mu$(Mo K$\alpha$) = 2.3 $cm^{-1}$. The cell dimensions and intensities were measured on a Syntex R3 four-circle diffractometer with graphite-monochromated Mo K$\alpha$ radiation with $\omega$-scan mode within $2\theta$ less than 50°. A total of 1805 independent reflections were collected, among which 1130 reflections ($I > 1.96\sigma(I)$) were stored as observed. The structure was solved by the direct method using MULTAN in Syntex XTL program.[15] A block-diagonal least-squares method was applied to the refinement with anisotropic temperature factors for all the non-hydrogen atoms. The $R$ value was 0.08. Atomic co-ordinates and thermal parameters, bond distances and angles, and the deviations of atoms from the least-squares planes are listed in Tables III, IV, and V (see the paragraph at the end of the paper about supplementary material concerning X-ray data tables for the compound 1′). The structure factor table (33 pages) is available from the author.

**Registry No.** 1, 73083-61-1; 1′, 91127-92-3; 2, 73083-59-7; 2′, 53996-55-7; 3, 91127-40-1; 4, 91127-41-2; 5, 91199-12-1; 6, 54053-51-9; 7, 91127-43-4; 8, 91156-92-2; 9, 73083-67-7; 10, 73083-65-5; 11, 73083-71-3; 12, 73083-69-9; 13, 91127-45-6; 14, 91127-47-8; 15, 91127-49-0; 16, 91127-51-4; 17, 91127-53-6; 18, 91127-55-8; 19, 91127-57-0; 20, 73083-87-1; 21, 73083-85-9; 22, 91127-59-2; 23, 91127-61-6; 24, 90133-33-8; 25, 90133-62-3; 26, 90133-64-5; 27, 73083-79-1; 28, 73083-77-9; 29, 91127-63-8; 30, 66571-82-2; 31, 66571-84-4; 32, 66571-86-6; 33, 91127-65-0; 34, 91127-67-2; 35, 91127-69-4; 36, 90133-42-9; 37, 91127-71-8; 38, 91127-72-9; 39, 73083-90-6; 40, 91127-74-1; 41, 35500-04-0; 42, 71031-54-4; 43, 41959-21-1; 44, 91127-75-2; 45, 91127-76-3; 46, 91127-77-4; 47, 91127-78-5; 48, 59181-69-0; 49, 91127-79-6; 50, 53512-25-7; 51, 90133-34-9; 52, 66572-01-8; 53, 91127-80-9; 54, 91127-81-0; 55, 90133-60-1; 56, 91127-82-1; 57, 91127-83-2; 58, 91127-84-3; 59, 91127-85-4; 60, 42528-40-5; 61, 91127-87-6; 62, 40020-62-0; 63, 42528-50-7; 64, 91127-88-7; 65, 91127-89-8; 66, 91127-90-1; 67, 91127-91-2; methyl iodide, 74-88-4; propyl bromide, 106-94-5; duryl bromide, 1646-53-3; diethyl malonate, 105-53-3; 3-(phenylthio)propyl bromide, 3238-98-0.

**Supplementary Material Available:** $^1H$ NMR spectra of 1 and 7 (Figure 2) and 9 and 10 (Figure 3), X-ray data tables for the compound 1′, atomic co-ordinates (x$10^4$) and thermal parameters for non-hydrogen atoms with their estimated standard deviations (Table III), bond distances (Å) and angles (deg) involving non-hydrogen atoms with their estimated standard deviations (Table IV), the deviations of atoms from the least-squares planes (Å) with their estimated standard deviations (Table V) (5 pages). Ordering information is given on any current masthead page.

(15) Mermain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A.* **1971**, *27*, 368.

# 3,8-Bis(trimethylsiloxy)-6-bromo-6,7-dihydro-1-phenyl-1*H*-phosphonin 1-Oxide and Its Conversion to a Phosphonin Oxide and a Cyclopenta-$\lambda^5$-phosphorin[1]

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*Received February 14, 1984*

Quantitative silylation of 5,6-dibromo-1-phenyl-3,8-phosphonanedione 1-oxide occurs with bis(trimethylsilyl)trifluoroacetamide, providing the 3,8-bis(trimethylsiloxy) derivative. Reaction of this water-sensitive compound with 1 equiv of triethylamine accomplishes elimination of HBr to give the title dihydrophosphonin derivative. Heating this compound in an inert solvent at 80 °C effects intramolecular ring closure with an accompanying silyl migration from C-O to P-O, providing the novel 1,3-bis(trimethylsiloxy)-1-phenylcyclopenta[*b*]-$\lambda^5$-phosphorin-7-one. Hydrolysis of this compound gave a crystalline diketo phosphoryl derivative of the bicyclic system. When the monobromo compound was reacted further with triethylamine, 3,8-bis(trimethylsiloxy)-1-phenyl-1*H*-phosphonin 1-oxide was formed along with the bicyclic product.

The bis(trimethylsilyl) ethers (1) of the bis(enolic) form of 3,8-phosphonane oxides[2] can be viewed as tetrahydrophosphonin derivatives, and are therefore of interest in synthetic work designed to achieve the fully unsaturated phosphonin system.[3] Such a synthesis would be facilitated by using 3,8-phosphonanediones that possess additional substituents on the ring in proper locations for elimination reactions. The 5,6-epoxy (2) and 5,6-dibromo (3) deriva-

(1) Taken from the doctoral dissertation of Rao, N. S., 1983. Supported by National Science Foundation Grant CHE-7717876.

(2) Quin, L. D.; Middlemas, E. D.; Rao, N. S. *J. Org. Chem.* **1982**, *47*, 905.

(3) Quin, L. D.; Rao, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 5960.

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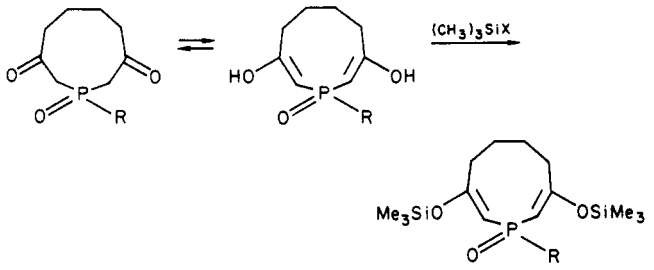
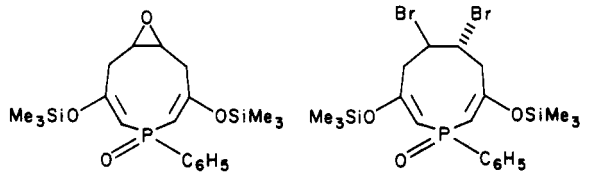


1a, R = $C_6H_5$
1b, R = $CH_3$

tives, both prepared in our previous work[2] as shown in Scheme I, are particularly attractive, and indeed some success has now been obtained with the dibromo derivative. Dehydrobromination reactions will be seen, however, to be complicated by an accompanying silyl migration and transannular ring closure.

Reaction of **2** and **3** with bis(trimethylsilyl)trifluoroacetamide (BSTFA) at mild temperatures (0–20 °C) in inert solvents such as ether, chloroform, or toluene provided complete conversion to the bis(trimethylsilyl) derivatives **4** and **5** as monitored by $^{31}P$ NMR spectral de-



4 5

terminations. The products were extremely sensitive to moisture, a severe handicap in plans to effect further conversion to the phosphonin system. Compound **4** has only been characterized by $^{13}C$ NMR spectroscopy and not further examined; compound **5** is of more interest and is the major subject of this paper.

$^{13}C$ NMR spectral data that support the assigned structures are provided in Table I; previously reported data[2] for compound **1a** are also provided for comparison. The dione (**2**) used for the preparation of **4** was a 3:1 mixture of diastereoisomers,[4] and such a mixture was obtained after the silylation. Isomers are not possible with the *trans*-5,6-dibromo substitution of **5**, but the $^{13}C$ NMR spectrum does show nonequivalence of carbons in comparable ring positions. This effect is present also in the diketone **3**,[4] and is attributed to a high inversion barrier for a nonplanar conformation. Useful for structure confirmation of **5** is the appearance of the signals for $sp^2$ carbons attached to phosphorus; these carbons are strongly shielded by electron release from the $Me_3SiO$ groups (to $\delta$ 100) and have quite large coupling constants to $^{31}P$ (124 and 140 Hz). Both double bonds must have the same geometry to give the spectra observed; the *E* structure is assigned, since *Z* is of prohibitively high energy. The $^{31}P$ NMR signals (Table I) for the series are quite similar (**1a**, +16.1;[2] **1b**, +20.3; **4**, +14.6; **5**, +19.2) and shifted upfield relative to a saturated phosphonane oxide (cf. **1b** +20.3, to 1-methylphosphonane 1-oxide, +48.9[2]). The dibromo compound **5** was also characterized by mass spectrometry, and gave a signal having the correct $M^+$ value (*m/e* 566) and the exact mass for $M^+ - CH_3$ (*m/e* 550.9661, calcd 550.9660).

The dibromo derivative **5** readily lost an equivalent of HBr when reacted overnight with 1 equiv of triethylamine

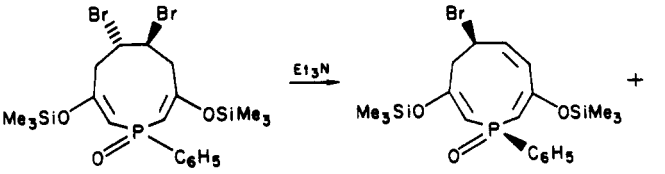
(4) Quin, L. D.; Middlemas, E. D.; Rao, N. S.; Miller, R. W.; McPhail, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 1893.

**Table I. $^{13}C$ NMR Spectral Data for Some Bis(trimethylsiloxy)phosphonin Derivatives[a]**

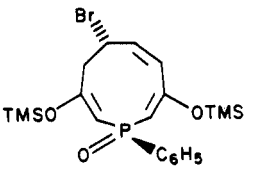
| | $\delta$ $^{13}C$ | | | |
|---|---|---|---|---|
| | C-2,9 | C-3,8 | C-4,7 | C-5,6 |
| **1a**[b] | 100.8 (115.2) | 170.3 (13.7) | 30.6[c] | 25.3 |
| **4**[d,e] | 103.5 (113.5) | 165.5 (12.2) | 34.2[c] | 35.5 |
| **5**[f,g] | 99.6 (140.4) | 164.0 (14.0) | 42.6 (3.1) | 53.4 |
| | 100.4 (123.9) | 167.4 (12.2) | 40.4 (6.1) | 53.0 |
| **7** | 97.3 (93.8) | 168.3 (14.7) | 131.6 (11.7) | 129.5 (5.9) |

[a] $^{13}C$–$^{31}P$ coupling constants (in Hz) are given in parentheses. [b] Previously reported.[4] [c] Small coupling not measured. [d] Major isomer only. [e] Phenyl $^{13}C$: ortho 129.2 (9.8), meta 128.7 (12.2), para 129.7 (2). [f] Phenyl $^{13}C$: 135.2 (105.4), ortho 129.7 (9.8), meta 128.9 (12.2), para 131.9 (2). [g] Spectrum published in ref 12.

at room temperature. The resulting dihydrophosphonin should exist in cis (**6a**) and trans (**6b**) forms with respect to the 1,5-substituents, and these were readily detected by the presence of two close lying signals on the $^{31}P$ NMR spectrum ($\delta$ +18.1 and + 17.4, 1:2, unassigned).



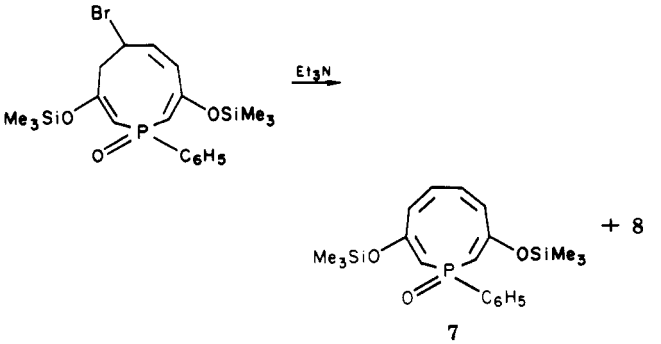
6a



6b

The mass spectrum, taken directly on the reaction product without removal of $Et_3N{\cdot}HCl$, gave the expected exact mass for the $M^+ + 1$ species; the base peak was $M^+ - CH_3$, with a strong $M^+ - Me_3Si$ peak. The $^{13}C$ NMR spectrum was complex due to the superposition of very similar signals for the two isomers. Only one of the new $sp^2$ carbons could be detected (C-5, $\delta$ 141.3 and 137.9); the second was mixed with the aromatic signals. Again hydrolytic instability prevented isolation of the product.

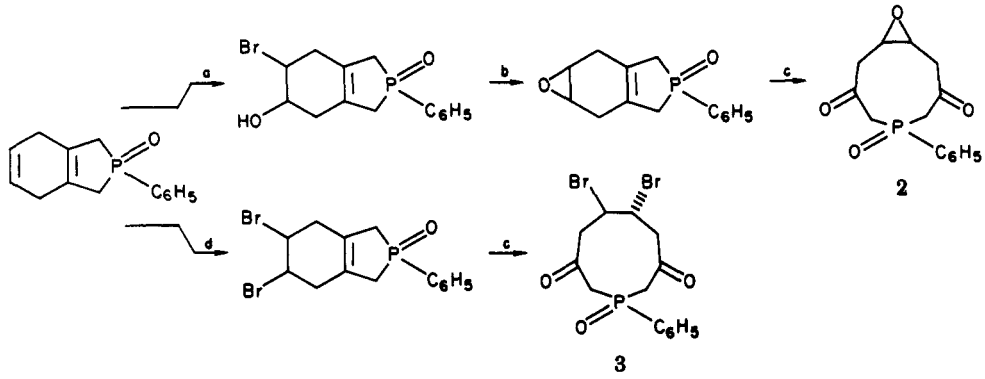
Dehydrohalogenation of **6** was accomplished by exposure to 1 equiv of triethylamine at room temperature for one week. Two products were formed in nearly equal amount. The product with $\delta$ $^{31}P$ NMR +30.3 was assigned the desired phosphonin oxide structure **7**. Its $^{13}C$ NMR spec-



7

trum (Table I), obtained by subtracting the spectrum of the second compound (**8**), showed the symmetry of the all-cis structure. The change in ring geometry allowed 3-bond coupling (11.7 Hz) to appear in this compound; in the tetrahydro derivatives, no coupling is observed. It is also notable that the $\pi$-system allows pronounced 4-bond

Scheme I[a]



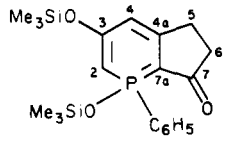
[a] (a) *N*-bromosuccinimide, $H_2O$; (b) NaOH; (c) $O_3$, -78 °C, then $(MeO)_3P$; (d) $Br_2$ in $CH_2Cl_2$.

coupling (5.9 Hz) to prevail. Only four ring carbon signals were observed, all in the $sp^2$ region. This result confirms the *Z* structure at C-4 and C-5 that was assigned previously to **6**, since the same olefinic structure must be formed in the second dehydrohalogenation as in the first to give the symmetry observed. Compound **7** required refrigeration for storage; it decomposed to a black tar on standing at room temperature for 2–3 weeks. The product appeared polymeric and gave no indication of the intramolecular [4 + 2] cycloaddition observed recently[3] for 1-phenylphosphonin oxide. Attempted hydrolysis of the siloxy groups also resulted in polymeric products, and attempts at P-deoxygenation with phenylsilane fared no better.

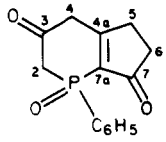
Although not isolatable in pure form, **7** is of significance as the first example of a monocyclic phosphonin oxide with proven all-cis structure. The 1-phenylphosphonin oxide prepared in other work[3] has a trans double bond at C-2,3; it also is unstable, requiring preservation at −15 °C.

Later experiments provided conditions for obtaining the second product (**8**) free of phosphonin **7**, thus facilitating the identification of both. Simply heating the dibromide **5** or the monobromide **6** in chloroform at 80 °C (sealed tube) for 6 h produced **8** quantitatively. This product had a peak in its mass spectrum with the same *m/e* value as the molecular ion of **7**, and therefore was also derived from loss of 2 mol of HBr. Since we had previously[2] observed an intramolecular alkylation occurring with the dibromophosphonanedione **3**, we suspected such a process had occurred in the formation of **8**, which would give rise to a bicyclic structure containing a phosphorin ring with a cyclopentane fused at the *b* face. Details of the substitution pattern of this unusual product emerged as NMR studies proceeded. Significant observations: (1) Two different types of trimethylsiloxy groups were present as revealed by $^{29}Si$ NMR spectroscopy (δ 26.0, 32.2). The latter was coupled to $^{31}P$ (3 Hz) and appeared attributable to a $Me_3Si$–O–P group as might occur from silyl migration from C–O. (2) In the $^{13}C$ NMR spectrum (Table II), two $sp^3$ carbons were present; both were coupled to $^{31}P$ by a magnitude (12–13 Hz) suggestive of a 3-bond connection. INEPT $^{13}C$ NMR experiments, which we have previously applied with great success to organophosphorus compounds,[5,6] revealed both signals to arise from methylene carbons which exhibited signal inversion at 3/(4*J*). (3) A carbonyl carbon, resulting from the $Me_3Si$ migration, was indicated by low-field $^{13}C$ signals (δ 201.2 in a concentrated solution). This carbonyl had a very low-frequency infrared stretching vibration (1560 $cm^{-1}$), resembling that seen in

**Table II. $^{13}C$ NMR Data[a] for 1,3-Bis(trimethylsiloxy)-1-phenylcyclopenta[*b*]-λ⁵-phosphorin-7-one (8)[b] and Its Hydrolysis Product 9**



8



9

| C | δ | $J_{PC}$ | δ | $J_{PC}$ |
|---|---|---|---|---|
| 2 | 75.5[c] | 121.1 | 36.9 | 68.9 |
| 3 | 169.7[e] | 14.6 | 200.7 | 4 |
| 4 | 98.4[c] | 2.9 | 31.6[f] | 11.7 |
| 4a | 155[g] | | 144.0 | 7.4 |
| 5 | 28.8[d] | 12.7 | 24.9 | 4.4 |
| 6 | 35.5[d] | 11.7 | 34.8[f] | 8.8 |
| 7 | 201.2[e] | 9.8 | 183.9 | 5.0 |
| 7a | 94.7[e] | 106.9 | *h* | |

[a] In $CDCl_3$ solution, 350 mg/mL. The signals of **8** (especially for C-7) show concentration dependence. Coupling constants in Hertz. [b] Phenyl signals: ipso 131.5 (106.1), ortho 132.2 (8.8), meta 128.4 (14.6), para 131.8 (2). [c] Intensified by INEPT with 2/4*J* delay. [d] Inverted by INEPT with 3/4*J* delay. [e] Suppressed by INEPT with 1/4*J* delay. [f] Could be reversed. [g] Tentative; mixed with trifluoroacetyl derivatives. [h] Overlaps with phenyl signals.

β-diketones,[7] where the monoenol form has a carbonyl stretch at 1540 $cm^{-1}$. (4) INEPT $^{13}C$ NMR experiments also revealed two of the $sp^2$ carbons to contain one H, and three to have no H. One of the tertiary carbons was at the abnormally high-field value of δ 75.5 and was directly bonded to P ($J_{PC}$ = 121.1 Hz). A combination of positive character on P and the high electron density of a β-enol ether carbon could account for this shift. The other C attached to P lacked a hydrogen and was also at relatively high field (δ 94.7, *J* = 106.9 Hz).

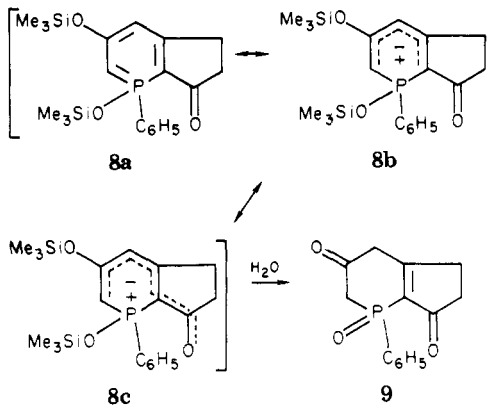
The structure (**8**) that best accommodates these facts has the unusual features of a λ⁵-phosphorin moiety in the bicyclic system. Delocalization in the λ⁵-phosphorin is expressed by resonance form **8b**, and extension into the carbonyl group by **8c**.

The proton NMR spectrum fits this structure; the two $CH_2$ groups gave signals at δ 2.4 and 2.9, while the olefinic protons showed the upfield shifting for location in the β-position of an enol ether. That olefinic proton on the carbon α to phosphorus gave a 4-line pattern from coupling to $^{31}P$ and to $H_4$.

Confirmation of this structure came from the hydrolysis to diketone **9**, which gave the correct elemental analysis and the expected $^{13}C$ NMR spectrum (Table II). An iso-

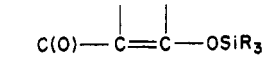
(5) Quin, L. D.; MacDiarmid, J. E. *J. Org. Chem.* **1982**, *47*, 3248.
(6) Quin, L. D.; Kisalus, J. C.; Mesch, K. A. *J. Org. Chem.* **1983**, *48*, 4466.

(7) See, for example, Sadtler Standard Infrared Grating Spectrum No. 48019P for 1,3-cyclohexandione.




mer of **9**, with the double bond in the 5,6-position, has been reported[2] from the base-promoted intramolecular reaction of dibromophosphonane **3**. Structure **8** is of interest as the first example of a $\lambda^5$-phosphorin bearing a fused cycloalkano ring. The $^{31}P$ shift of $\delta$ + 27.8 compares well with that of a monocyclic phosphorin (1,4-diphenyl-1-methoxy-$\lambda^5$-phosphorin,[8] $\delta$ +38.3).

A possible mechanism for the formation of **8** is shown as Scheme II. An important step is the transfer of trimethylsilyl from the C–O group to the phosphoryl oxygen. Although there is no exact precedent for such a reaction with a phosphine oxide, transfer of silyl groups to carbonyl oxygen have been reported[9] in the related system



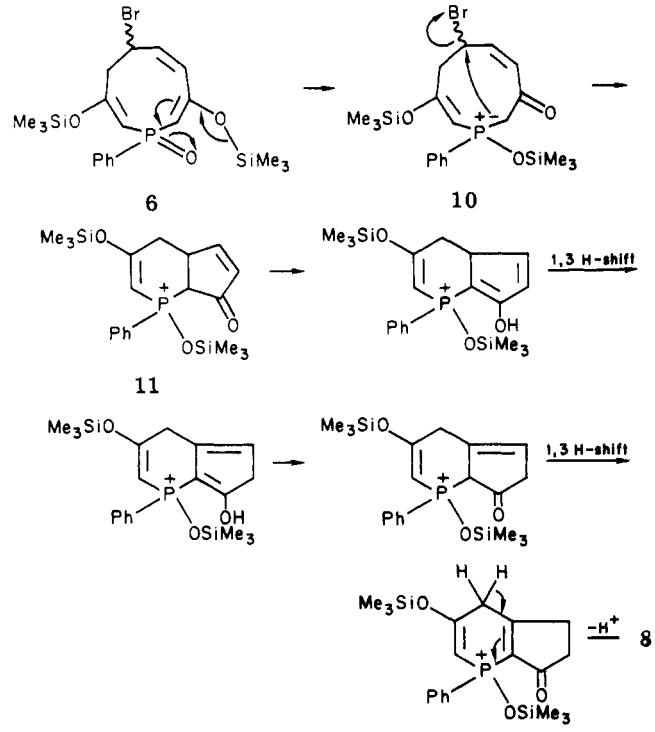

and phosphoryl oxygen of a phosphonate has been proposed recently[10] to accept a silyl group from an $\alpha$-siloxy substituent. The electron-rich C-2 of **10** then attacks the carbon bearing bromine to form the bicyclic system **11**. The events involving proton shifts by which the $\lambda^5$-phosphorin system is established are uncertain, but a reasonable sequence might involve two 1,3-shifts, possibly through the enol, to form the 1,4-dihydrophosphorin system **12**, and then loss of a proton.

## Experimental Section[11]

**3,8-Bis(trimethylsiloxy)-5,6-epoxy-1-phenyl-4,5,6,7-tetrahydro-1*H*-phosphonin 1-Oxide (4).** A mixture of dione **2**[4] (0.20 g, 0.72 mmol), $CDCl_3$ (0.5 mL), and BSTFA (0.9 mL, 3.4 mmol) under nitrogen was heated at 60 °C for 1 h. The resulting pale yellow solution was carefully concentrated to give **4** as a pale, viscous oil; $^{31}P$ NMR ($CDCl_3$) $\delta$ +14.6 as the only signal; $^{13}C$ NMR ($CDCl_3$), Table I.

**3,8-Bis(trimethylsiloxy)-5,6-dibromo-1-phenyl-4,5,6,7-tetrahydro-1*H*-phosphonin 1-Oxide (5).** To a suspension of dione **3**[4] (0.49 g, 1.16 mmol) in 2 mL of $CDCl_3$ was added BSTFA (1.2 mL, 4.5 mmol) and the mixture stirred under dry nitrogen for 18 h at 0 °C. During this time the solid dissolved to give a yellow solution. A $^{31}P$ NMR spectrum of an aliquot showed complete consumption of the dione and one new signal at $\delta$ +19.2. The reaction mixture was then carefully concentrated (avoiding moisture) under vacuum giving **5** as a viscous, yellow oil: $^1H$ NMR ($CDCl_3$) 2.60–3.00 (m, $CH_2$), 4.55–5.17 (m, CH), 6.1 (d, $^2J_{PH}$ = 15 Hz, =CH), 7.40–7.85 (complex m, phenyl H); $^{31}P$ NMR ($CDCl_3$) $\delta$ +19.2; $^{13}C$ NMR ($CDCl_3$), Table I; mass spectrum calcd for $M^+ - CH_3$, $m/e$ 550.9660, found 550.9661.

Scheme II




**3,8-Bis(trimethylsiloxy)-6-bromo-1-phenyl-6,7-dihydro-1*H*-phosphonin 1-Oxide (6).** The dibromide **5** obtained by the reaction of 0.49 g (1.16 mmol) of dione **3** with BSTFA (1.2 mL, 4.52 mmol) in $CDCl_3$ (3 mL) as above was treated with triethylamine (0.12 g, 1.16 mmol) and the mixture stirred at room temperature under a dry atmosphere overnight. The reaction mixture was centrifuged and the supernatant liquid transferred to a dry container and concentrated. The resulting light brown oil was determined spectroscopically to consist of the desired compound **6** as a mixture of diastereoisomers: $^{31}P$ NMR ($CDCl_3$) $\delta$ +17.4, +18.1 (2:1); $^{13}C$ NMR ($CDCl_3$) major isomer $\delta$ 41.8 (C-7), 44.9 (C-6), 103.9 (d, 113.2, C-2 or C-9), 107.9 (d, 117.3, C-2 or C-9), 137.9 (C-5), 165.7 (d, 10.1, C-3 or C-8), 164.5 (d, 11.2, C-3 or C-8), minor isomer 44.1 (C-7), 45.6 (C-6), 104.5 (d, 117.3 Hz, C-2 or C-9), 109.4 (d, 117.2 Hz, C-2 or C-9), 141.3 (C-5), other signals overlapped; mass spectrum calcd for $M^+ + 1$, $m/e$ 485.0732, found 485.0731.

**Rearrangement of 5 and 6 to 1,3-Bis(trimethylsiloxy)-1-phenylcyclopenta[*b*]-$\lambda^5$-phosphorin-7-one (8).** Heating a chloroform (5 mL) solution of the dibromo derivative **5** or the monobromo **6** (1.16 mmol) at 80 °C in a sealed tube (free of moisture) for 6 h provided the bicyclic compound **8** quantitatively as determined by $^{31}P$ NMR. The reaction mixture was concentrated under high vacuum and provided **8** as a red-brown oil: $^1H$ NMR ($CDCl_3$) $\delta$ 2.4 (m, 2 H, $CH_2$), 2.9 (m, 2 H, $CH_2$), 4.4 (d of d, $^2J_{PH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, HC-2), 5.35 (s, HC-4), 7.4–7.9 (m, 5 H, phenyl H); $^{31}P$ NMR ($CDCl_3$) $\delta$ +27.8; $^{13}C$ NMR ($CDCl_3$), Table II; $^{29}Si$ NMR ($CDCl_3$) $\delta$ 32.2 (d, $^2J_{PSi}$ = 3 Hz), 26.0; IR (neat) 1540 $cm^{-1}$ ($\nu_{C=O}$); mass spectrum calcd for $M^+$, $m/e$ 404.1380, found 404.1381.

**1-Phenylcyclopenta[*b*]-$\lambda^5$-phosphorin-3,7-dione 1-Oxide (9).** The sample of **8** prepared above was hydrolyzed by treatment of a chloroform solution (40 mL) with ice cold 2 N $H_2SO_4$ solution (40 mL) for 0.75 h. The layers were separated, the aqueous layer extracted with chloroform (3 × 40 mL), and the combined extract dried ($MgSO_4$). The brown residue remaining from concentration was triturated with chloroform and the white solid that resulted was filtered and dried: $^1H$ NMR ($CDCl_3$) $\delta$ 2.25–2.55 (m, 2 H), 2.70–2.95 (m, 2 H), 2.95–3.70 (m, 4 H, $H_2C$-2 and $H_2C$-4), 7.40–7.90 (m, 5 H, phenyl H); $^{31}P$ NMR ($CDCl_3$) $\delta$ +19.8; $^{13}C$ NMR, Table

(8) Märkl, G.; Liebl, R.; Hüttner, A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 528.
(9) Reich, H. J.; Murcia, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 3418.
(10) Sekine, M.; Futatsugi, T.; Hata, T. *J. Org. Chem.* **1982**, *47*, 3453.
(11) Proton NMR FT spectra were obtained with a Bruker NR-80 spectrometer. Carbon-13 NMR FT spectra (including the INEPT sequence) were taken on a JEOL FX-90Q spectrometer at 22.5 MHz. Phosphorus-31 NMR FT spectra were obtained with the FX-90Q at 36.2 MHz; chemical shifts are expressed in ppm relative to external 85% $H_3PO_4$ with positive shifts downfield. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Special care in drying apparatus and solvents, and in protecting reaction mixtures and products with a dry nitrogen atmosphere, was required in these experiments.
(12) Spectrum No. 846, "Selected $^{13}C$ Nuclear Magnetic Resonance Spectral Data"; Thermodynamics Research Center: Texas A and M University, College Station, TX, Supplementary Volume G-12.

II; IR (Nujol) 1670 (strong), 1710 (medium) $cm^{-1}$. Anal. Calcd for $C_{14}H_{13}O_3P$: C, 64.62; H, 5.05; P, 11.90. Found: C, 64.66;, H, 4.95; P, 11.90.

**3,8-Bis(trimethylsiloxy)-1-phenyl-1*H*-phosphonin 1-Oxide (7).** To a solution of crude monobromide 6 (1.2 mmol) in $CDCl_3$ (2 mL) at 0 °C was added triethylamine (0.24 g, 2.4 mmol) and the mixture stirred at 0 °C for 48 h. The reaction mixture was centrifuged and the supernatant solution carefully removed (avoiding exposure to moisture) and concentrated under high vacuum. The resulting dark oil consisted of a 1:1 mixture of 7 and 8, which could not be separated without hydrolysis occuring. Spectral properties of 7 were determined by deleting the signals due to 8: $^1H$ NMR ($CDCl_3$) $\delta$ 4.5–5.7 (complex m, 6 H), 7.4–7.9 (m, 5 H, phenyl H); $^{31}P$ NMR ($CDCl_3$) $\delta$ +30.3; $^{13}C$ NMR ($CDCl_3$), Table I.

**Registry No.** 2 (isomer 1), 80794-96-3; 2 (isomer 2), 80794-95-2; 3, 75531-99-6; 4 (isomer 1), 90991-51-8; 4 (isomer 2), 91050-47-4; 5, 90991-52-9; 6a, 90991-49-4; 6b, 91050-46-3; 7, 90991-53-0; 8, 91002-47-0; 9, 90991-50-7; BSTFA, 21149-38-2.

# Transition-State Structures for the Hydrolysis of Cyclic and Acyclic Carbonates[1]

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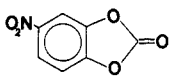
The hydrolysis of *o*-(4-nitrophenylene) carbonate (1) is third order in water while the hydrolysis of bis(4-nitrophenyl) carbonate (2) is second order in water. Proton inventories for both are downwardly curved indicating contributions by more than one proton to the observed kinetic solvent deuterium isotope effects of $k_{H_2O}/k_{D_2O}$ = 2.46 and 2.20 for 1 and 2, respectively. The transition-state structure appears to involve a cyclic array of three water molecules in the case of 1, the cyclic carbonate. The transition-state structure for hydrolysis of the acyclic carbonate 2 involves only two water molecules with one acting as a general base to remove a proton from the nucleophilic water molecule. This has been referred to as a catalytic proton bridge transition state. Deslongchamp's theory of stereoelectronic control has been applied to an analysis of the proton inventories for the water-catalyzed hydrolysis of a cyclic and an acyclic carbonate ester.

## Introduction

In order to fully delineate the mechanism of biological hydrolytic reactions it is necessary to understand their nonbiological analogues in extreme detail. Study of the hydrolytic ring opening of certain cyclic esters and comparison of the results with those for the hydrolytic cleavage of the corresponding acyclic esters may provide additional insight into the mechanisms which can serve as models for many biological systems.[3] With this in mind, Fife and McMahon[4] have extensively investigated the hydrolysis of *o*-(4-nitrophenylene) carbonate (1) and bis(4-nitrophenyl) carbonate (2). We report here a study of the pH



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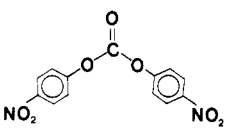

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independent, water-promoted hydrolysis of 1 and 2 in mixtures of protium oxide and deuterium oxide. Such a study constitutes a proton inventory and allows us to suggest likely roles for the water molecules in the transition states for these hydrolysis reactions.

## Results

The hydrolysis of 1 and 2 has been studied at pH 3.0, or the equivalent point on the pH(D) rate profile, in protium oxide, deuterium oxide, and mixtures of the two. Table I and Figure 1 show the dependence of the observed first-order rate constants for the hydrolysis of 1 on the isotopic composition of the solvent system of atom fraction

**Table I. First-Order Rate Constants for the Water-Catalyzed Hydrolysis of *o*-(4-Nitrophenylene) Carbonate (1) in $H_2O$–$D_2O$ Mixtures of Atom Fraction Deuterium ($n$) at 25.05 ± 0.05 °C at pH(D) 3[a]**

| | | $10^6 k_n$, $s^{-1}$ | |
|---|---|---|---|
| $n$ | no. of runs | obsd | calcd[b] |
| 0.000 | 5 | 8038 ± 11[c] | 8038 |
| 0.247 | 5 | 6612 ± 34 | 6629 |
| 0.494 | 5 | 5390 ± 22 | 5369 |
| 0.741 | 5 | 4235 ± 17 | 4253 |
| 0.988[d] | 4 | 3273 ± 13 | 3271 |

[a] The pH(D) was maintained at 3.0 by using HCl or DCl. The ionic strength was kept at 0.2 M with potassium chloride. The volume percentage of acetonitrile for each run was 0.83%. [b] Calculated on the basis of eq 6 with $\phi_a^*$ = 0.565 and $\phi_b^*$ = 0.843. [c] Error limits are standard deviations. [d] Atom fraction of deuterium in "pure" $10^{-3}$ M DCl in $D_2O$ as determined by Josef Nemeth.[43]

**Table II. First-Order Rate Constants for the Water-Catalyzed Hydrolysis of *o*-(4-Nitrophenylene) Carbonate (1) in Acetonitrile Containing 8 M $H_2O$–$D_2O$ Mixtures of Atom Fraction of Deuterium ($n$) at 50.05 ± 0.05 °C at pH(D) 3[a]**

| | | $10^7 k_n$, $s^{-1}$ | |
|---|---|---|---|
| $n$ | no. of runs | obsd | calcd[b] |
| 0.000 | 5 | 5194 ± 35[c] | 5194 |
| 0.247 | 5 | 4351 ± 22 | 4311 |
| 0.494 | 5 | 3492 ± 12 | 3506 |
| 0.741 | 5 | 2783 ± 9 | 2775 |
| 0.988 | 5 | 2125 ± 9 | 2116 |

[a] The pH(D) was maintained at 3.0 by using HCl or DCl. The ionic strength was not maintained constant. [b] Calculated on the basis of eq 6 with $\phi_a^*$ = 0.515 and $\phi_b^*$ = 0.883. [c] Error limits are standard deviations.

(1) Support of this work by the Robert A. Welch Foundation is gratefully acknowledged.

(2) On leave from Presidency College, Madras, India.

(3) Kaiser, E. T.; Kezdy, F. J. In "Progress in Bioorganic Chemistry"; Kaiser, E. T.; Kezdy, F. J., Eds.; Wiley: New York, 1979; Vol. 4.

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