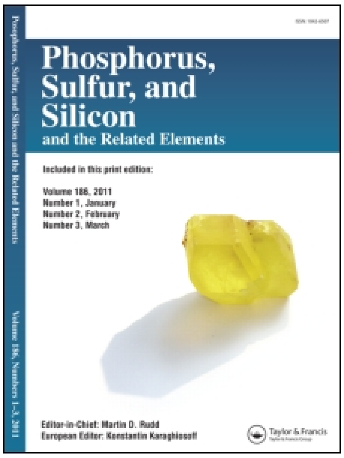

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VICINAL DIBROMO-1-HYDROXYPHOSPHOLANE 1-OXIDES

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VICINAL DIBROMO-1-HYDROXYPHOSPHOLANE 1-OXIDES

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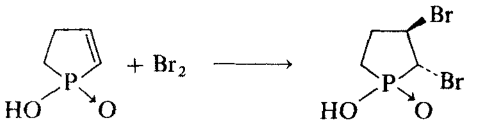
2,3-Dibromo-1-hydroxyphospholane 1-oxide and 3,4-dibromo-1-hydroxyphospholane 1-oxide were prepared in high yield by bromine addition to 1-hydroxyphosphol-2-ene 1-oxide or 1-hydroxyphosphol-3-ene 1-oxide, respectively. Both compounds were characterized by ^{1}H, ^{31}P and ^{13}C nmr, IR, Laser Raman and mass spectrometry.

INTRODUCTION

In an earlier communication[1] we have reported the preparation and characterization of isomerically pure samples of 1-hydroxyphosphol-2-ene 1-oxide and 1-hydroxy-phosphol-3-ene 1-oxide. In the course of our studies of derivatives of these compounds we are describing in the present paper the preparation and spectroscopic characterization of the bromine addition products of the above 1-hydroxyphospholene 1-oxides.

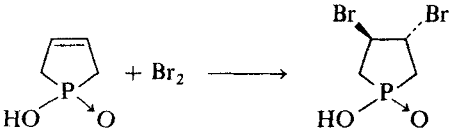
RESULTS AND DISCUSSION

The addition of elemental bromine to the olefinic double bond in 1-hydroxyphospholene 1-oxides proceeds smoothly and in high yield to produce the corresponding dibromo-1-hydroxyphospholane 1-oxides.



(1)

I



(2)

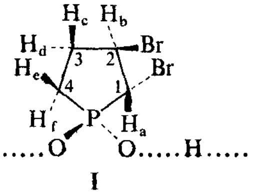
II

In agreement with the generally accepted mechanism[2] of bromine addition to double bonds in cyclo-olefins via a bromonium ion intermediate, the two bromine atoms in the adducts **I** and **II** are placed in *trans*-position to each other.

Due to hydrogen bonding the phosphorus atom in both compounds is *not* a chiral center and, therefore, bromine addition to the phosphol-2-ene in Eq. (1) results in only *one* isomer. In related compounds where the phosphorus atom in the ring does represent a chiral center, *e.g.* in 2,3-dibromo-1-phenylphospholane 1-oxide where the OH group in I has been replaced by C_6H_5, two stereoisomers indeed are formed and both have been isolated and characterized.[3,4] It has been shown that for the two isomers the α-bromine atom (on the carbon atom next to phosphorus) may be either in *cis* or *trans*-position relative to the phenyl group on phosphorus. However, no such isomerism is realized in the present 1-hydroxy derivative.

Proton Nmr Spectra

In interpreting the proton nmr spectra of the two isomers of dibromo-1-hydroxyphospholane 1-oxide it is helpful to consider the spatial arrangement of the protons in the 5-membered ring and to keep in mind that the phosphorus atom in the present case, due to hydrogen bonding, no longer is a chiral center. In a single crystal X-ray diffraction study of the related 1-hydroxyphospholane 1-oxide[5] it was shown that in the solid state the molecules are arranged in helices around a screw axis and are bonded together through hydrogen bonds between the OH group of one molecule and the oxo atom of the next. Hydrogen bonding is also assumed to be effective in solution, probably in a similar fashion as observed for carboxylic acids. Furthermore, it was stated in that study that the four atoms P, C_1, C_3 and C_4, are lying nearly in a plane with C_2 (a β-C atom) at the flap when expressing the conformation as resembling that of an envelope.



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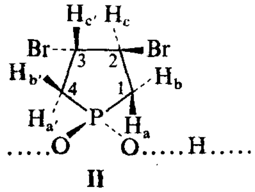


II

The proton spectra of the isomer I are shown in Figure 1. The molecule represents a seven spin system with six different proton environments, which, at 60 MHz, results in two sets of multiplets, at 3.9–4.6 ppm (CH) and 1.6–3.2 ppm (CH_2), and a singlet for the OH proton at 5.7 ppm. At 90 MHz the CH protons appear to approach separation into two sets of multiplets with ^{31}P-decoupling resulting in some simplification of the spectra. However, only at 270 MHz clear separation into sets of multiplets representing the six different proton environments is seen. In the latter spectra the most downfield multiplet centered at 4.3 ppm represents the proton H_b with the multiplicity caused by coupling to H_a, H_c, H_d and P. The proton H_a is represented by the triplet centered at 4.05 ppm (J = 7.4 Hz) which actually is a doublet of doublets resulting from coupling to H_b and P and accidental overlap occurring due to the similarity of the two effective coupling constants $^{2}J_{H_aH_b}$ and $^{2}J_{H_aP}$. In the CH_2-region the multiplets centered at 2.7 and 2.0 ppm each represent one proton and the multiplet at 2.25 corresponds to two protons of the two CH_2 groups of the molecule.

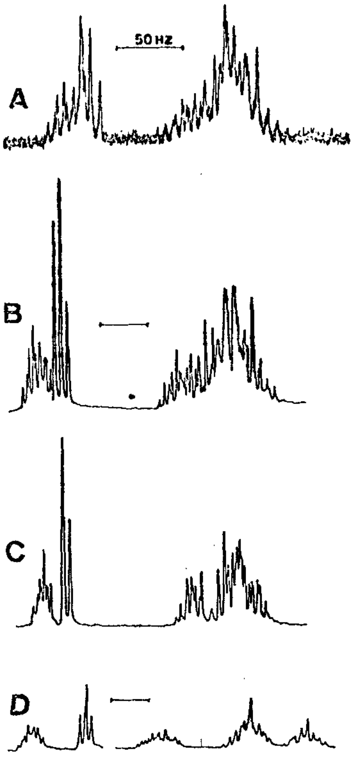


FIGURE 1 Proton nmr spectra (in $CDCl_3$) of 2,3-dibromo-1-hydroxyphospholane 1-oxide at various magnetic fields; A, 60 MHz; B, 90 MHz; C, 90 MHz, ^{31}P-decoupled; D, 270 MHz. The scale in all cases represents 50 Hz.

The proton nmr spectra of the isomer II are shown in Figure 2. The symmetry of the molecule is reflected in the first order spectra seen at higher magnetic fields. Although spectra taken at 60 MHz display considerable overlap, the ones taken at 90 MHz allow an interpretation of the multiplicity, assuming, for practical purposes, the equivalency of H_a and $H_{a'}$, H_b and $H_{b'}$, and H_c and $H_{c'}$. The doublet of triplets in the 90 MHz spectrum centered at 4.7 ppm is an AMNX spectrum (M = H_a, N = H_b and X = P) representing the CH protons which upon ^{31}P-decoupling collapse to a triplet thus allowing determination of the coupling constant $^{3}J_{H_cP} = 16.6$ Hz. Due to the

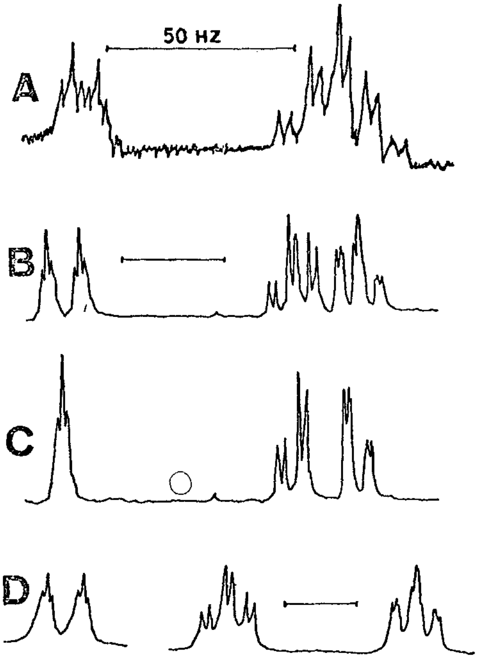


FIGURE 2 Proton nmr spectra (in $CDCl_3$) of 3,4-dibromo-1-hydroxyphospholane 1-oxide of various magnetic fields; A, 60 MHz; B, 90 MHz; C, 90 MHz, ^{31}P-decoupled; D, 270 MHz. The scale in all cases represents 50 Hz.

TABLE I

Summary of proton nuclear magnetic resonance data for the two isomeric dibromo-1-hydroxyphospholane 1-oxides (see text for interpretation)

Compound I		Compound II	
δ(ppm)	Assignment	δ(ppm)	Assignment
4.05, t, H, J = 7.4 Hz	H_a	4.7, dt, 2H J = 16.6 Hz, J = 3.5 Hz	H_c
4.3, m, H	H_b		
2.7, m, H 2.25, m, 2H 2.0, m, H	CH_2	2.9, m, 2H J = 10.7, J = 3.8, J = 10.7 2.4, m, 2H	CH_2

We also obtained 500 MHz proton nmr spectra of I and II, as shown in Fig. 3, however, except for better resolution, no additional information may be gained.

similarity of the coupling constants $^3J_{H_cH_a} \approx {}^3J_{H_cH_b} \approx 3.5$ Hz this triplet is a result of an accidentally overlapping doublet of doublets. The multiplets centered at 2.9 and 2.4 ppm representing CH_2 protons may be approximated as the AB part of an ABMX spectrum ($M = H_c$, $X = P$) which upon ^{31}P-decoupling turns into the AB part of an ABM spectrum. This then allows an estimation of some of the coupling constants. From the downfield multiplet centered at 2.9 ppm one may determine $^2J_{HP} = 10.7$ Hz, $^2J_{HH_c} = 3.8$ Hz (H may be either H_a or H_b) and $^2J_{H_aH_b} = 10.7$. The upfield multiplet centered at 2.4 ppm is of similar structure, however, in this case higher order effects are seen and an estimation of coupling constants is less accurate. Nevertheless, the same basic pattern as seen for the 2.9 multiplet is displayed by the multiplet at 2.4 ppm. Based on the available data we cannot state which of the multiplets represents the H_a and which the H_b protons. A summary of the proton nmr data is presented in Table I.

^{31}P Nmr Spectra

The ^{31}P nmr chemical shifts of the 2,3-dibromophospholane derivative at 58.5 ppm (downfield shifts are positive and were referenced versus 85% H_3PO_4) and of the 3,4-dibromophospholane at 54.4 ppm are at the low-field end of the range normally found for phosphinic acids.[6] These shifts are upfield of the corresponding precursor 1-hydroxyphospholene 1-oxides[1] (2-isomer: 76.8 ppm and 3-isomer: 75.1 ppm).

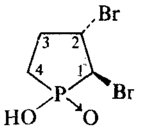
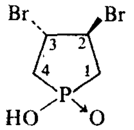
In proton-coupled ^{31}P nmr spectra the resonance for the 2,3-isomer is a broad signal without any significant fine structure. For the 3,4-dibromo isomer, as the more symmetric molecule, this ^{31}P resonance is a fairly well resolved multiplet displaying at least 9 resolved lines. Assuming first order effects one expects 27 resonances which, however, due to overlap on account of the similarity of the two coupling constants $^2J_{H_aP} \approx {}^2J_{H_bP} \approx 10.7$ Hz, would not all be resolved.

^{13}C Nmr Spectra

All ^{13}C nmr resonances of the two dibromophospholane derivatives are doublets due to ^{13}C-^{31}P nuclear spin coupling as shown in Table II. The assignment of the resonances in Table II is based on off-resonance decoupling experiments which permit identification of the resonance due

TABLE II

^{13}C Nmr Chemical shifts[a] and ^{13}C-^{31}P nuclear spin coupling coupling constants (in Hz) of the two isomers of dibromo-1-hydroxyphospholane 1-oxide

		
C-1	45.65(88.2)	35.31(89.9)
C-2	50.97(27.9)	49.58(12.7)
C-3	31.27(4.4)	49.58(12.7)
C-4	24.00(94.1)	35.31(89.9)

[a] Spectra were recorded on a FT Bruker WH-60 spectrometer operating at 15.09 MHz at room temperature and were proton decoupled. The lock signal was derived from $CDCl_3$ used as solvent; chemical shifts were measured versus TMS, with downfield shifts being positive; coupling constants are listed in parentheses. Off-resonance spectra were obtained on a JOEL FX-100 nmr spectrometer

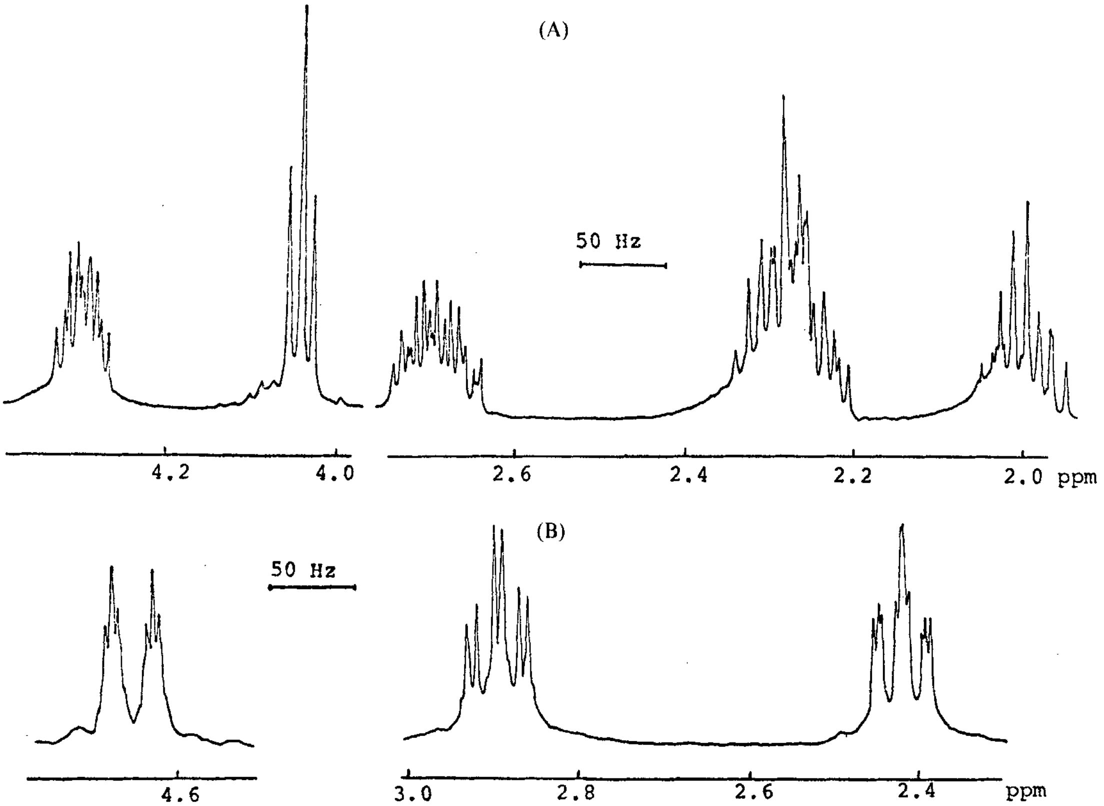


FIGURE 3 500 MHz proton Nmr spectra of (A) 2,3-dibromo-1-hydroxyphospholane 1-oxide and (B) 3,4-dibromo-1-hydroxyphospholane 1-oxide.

to CH_2 (each resonance forms a triplet) and CH (each resonance forms a doublet) groups and on the ^{13}C-^{31}P coupling constants, with the carbon atoms next to phosphorous having larger coupling constants than carbon atoms one atom removed from phosphorus.

In the 3,4-dibromophospholane, again, due to the absence of chirality at phosphorus, the carbon atoms C-1 and C-4 as well as C-2 and C-3 are stereochemically equivalent resulting in only two sets of doublets which were assigned on the same basis as above. It is of interest here to point out that in the corresponding tertiary phosphine oxides[3] C-1 is not equivalent to C-4, and C-2 is not equivalent to C-3 resulting in four sets of doublets owing to the chirality of phosphorus in the compounds. The $^{2}J_{PC-2}$ coupling constant for the 2,3-dibromo compound is quite large for a 2-bond coupling constant which generally is not larger than about 10 Hz in compounds of tetracoordinated P. Also in the related 2,3-dibromo-1-phenylphospholane 1-oxides[3] this coupling constant is extraordinarily large, 19.8 and 22.5, respectively. At this time, however, we have no explanation for these observations, it may be conceivable that the coupling pathway is 3-bond (going the other way in the ring) in which case such values may be achieved and where steredependency is realized or that conformational differences in solution are playing a role.

IR and Laser Raman Spectra

The spectra of the two dibromophospholane 1-oxides are shown in Figures 4 and 5, respectively. Characteristic features are the CH-stretching vibrations in the range 2900–3000 cm^{-1}, the five broad bands typical for the P-O-H group at 2525 to 2725, 2080 to 2350, 1600–1740, 917 to 1040 and 450–540, with the band at 1600–1740 being the strongest as seen in other phosphinic acids,[7] the P=O valence vibrations at 1228 (for I) and 1178 (for II), ring breathing vibrations at 838 (for I) and 806 (for II), in the Raman spectra and the very

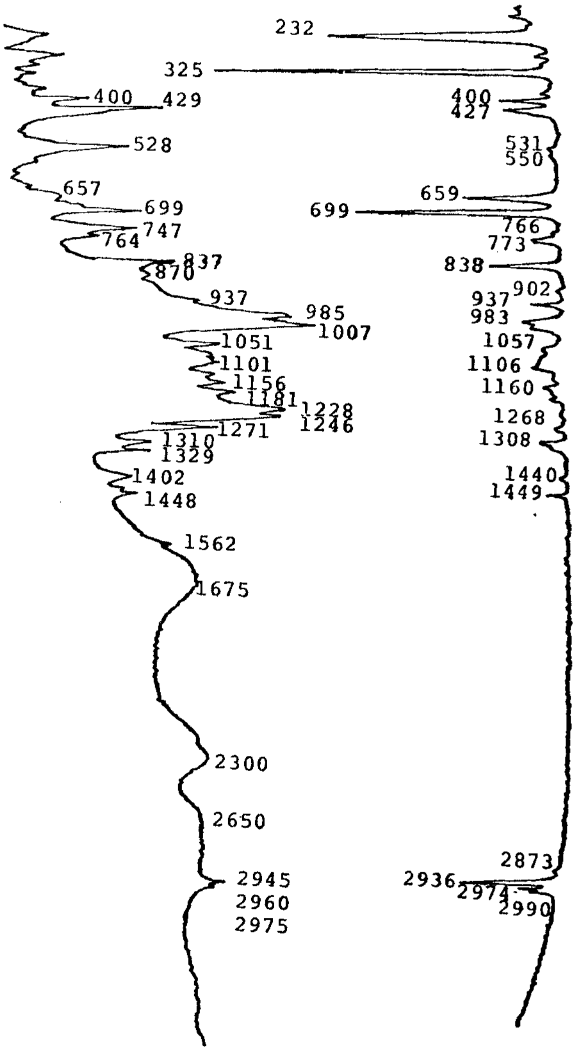


FIGURE 4 IR (left) and Laser Raman, (right) spectra of 2,3-Dibromo-1-hydroxyphospholane 1-Oxide obtained on a Beckman IR-12 (CsI pellet) and a Spex Ramalog 5 Laser Spectrometer (argon laser with 100 mW power light output), respectively.

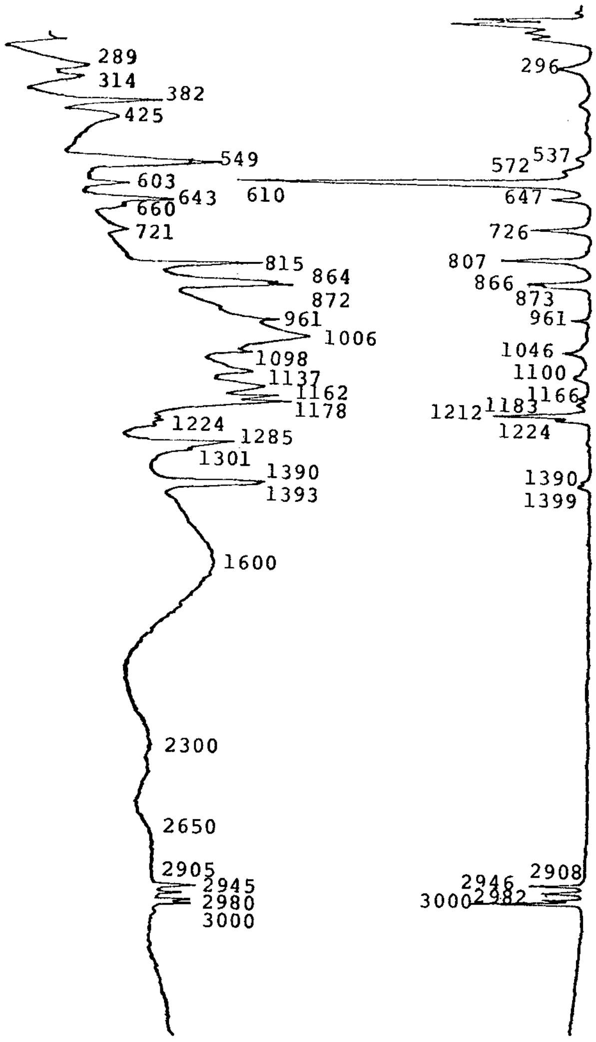


FIGURE 5 IR (left) and Laser Raman, (right) spectra of 3,4-Dibromo-1-hydroxyphospholane 1-Oxide obtained as described in Figure 4.

strong Raman lines at 699 (I) and 610 (II) for the C-Br stretching vibrations.

Mass Spectra

The fragmentation patterns of the two dibromo-1-hydroxyphospholane 1-oxides in Figure 6 show the molecular ions at m/e 276, 278 and 280 (due to the presence of the two isotopes ^{79}Br and ^{81}Br in about equal amounts) and the corresponding $M^+ + 1$ peaks at m/e 277, 279 and 281. The latter appearing at higher intensities than the corresponding M^+ peaks are seen quite frequently in mass spectra of organophosphorus acids[8,9] and are the result of ion molecule reactions and/or the presence of ^{13}C. The $M^+ + 1$ peaks are quite prominent for the two compounds in chemical ionization and field desorption ionization mass spectra. In both compounds in Figure 5 the ions due to loss of Br are of very high intensity, m/e 197 and 199, with these ions being the base peaks in the 2,3-dibromo compound. Other significant ions are m/e 117 ($M^+ - 2$Br,H), 108 and 106 ($BrCHCH_2$)$^+$, 71 ($CH{=}CHCH_2CH_2OH$)$^+$, which is the base

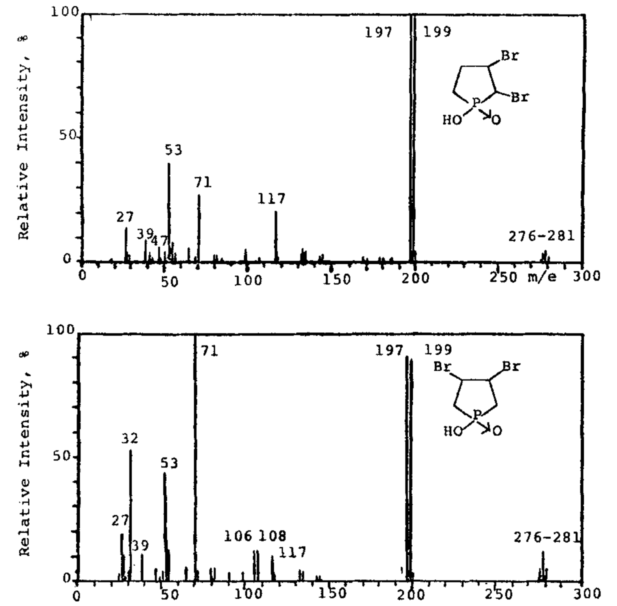


FIGURE 6 Mass spectra of Dibromo-1-hydroxyphospholane 1-Oxides at 70 eV (Varian-MAT CH-7; source: 250°; probe: 100°).

peak for the 3,4-dibromo compound, and 53 $(C_4H_5)^+$ which is the result of loss of water from m/e 71.

EXPERIMENTAL PART

Materials

1-Hydroxyphosphol-2-ene 1-oxide and 1-hydroxyphosphol-3-end 1-oxide were prepared as reported previously.[1]

2,3-Dibromo-1-hydroxyphospholane 1-oxide To a stirred solution of 32.2 g (0.274 mol) of 1-hydroxyphosphol-2-ene 1-oxide in 250 mL of chloroform kept at 0° was added dropwise a solution of 46.0 g (0.288 mol) of bromine in 50mL of chloroform resulting in a slightly exothermic reaction. After completed addition the dark red solution was slowly warmed to room temperature and let stand at this temperature over night. Proton nmr of a sample taken at this point showed that no olefinic protons were present indicating complete reaction. Subsequently, the volatiles were removed on a rotary evaporator resulting in a dark orange oil. Redissolution in chloroform/ethanol and addition of hexane resulted in 2 layers with the lower one crystallizing upon cooling with Dry Ice to give 85.7 g of crude product. This was dissolved in 50 mL of ethanol and 50 mL of hexane was added to produce, after standing in the refrigerator for a few days, 22 g of a crystalline product, mp 119–121°. From the filtrate, additional crops of crystals were obtained, 2nd fraction (from EtOH/hexane) 9.8 g, mp 115–121°, 3rd fraction (from $CHCl_3$ after charcoal treatment) 8.25 g, mp 118–120° and the 4th fraction (from $CHCl_3$) 23 g, mp 105–110°. Total yield 62.45 g (0.225 mol) or 82%. The first fraction was recrystallized from chloroform (10 g/30 mL, 75.5% recovery) to give the analytical sample, mp 124–125°, $\delta^{31}P$ ($CDCl_3$) 58.5 ppm.

Anal. Calcd for $C_4H_7Br_2O_2P$: C, 17.29; H, 2.54; Br, 57.51; P, 11.15; MW, 277.9. Found: C, 17.14; H, 2.60; Br, 57.21; P, 10.99; MW (by titration), 279.

3,4-Dibromo-1-hydroxyphospholane 1-oxide Following the procedure described above, 117.6 g (0.85 mol) of 1-hydroxyphosphol-3-ene 1-oxide in 600 mL of chloroform was reacted with 143.9 g (0.90 mol) of bromine dissolved in 100 mL of chloroform. After standing for a few days at room temperature, the solution upon evaporation yielded 254 g of crude solid product. This was dissolved in 850 mL of hot ethanol and 1700 mL of hexane was added. Upon standing over night 155.7 g of a crystalline material was obtained, mp 142–143°. The filtrate yielded a second fraction upon cooling with Dry Ice, 42.5 g, mp 137–140°. Total yield 198.2 g (0.71 mol) or 83.9%. Part of the first fraction was recrystallized from methanol (10 g/35 mL, 78% recovery) to give the analytical sample, mp 142–143°, $\delta^{31}P$ (DMSO-d_6) 54.4 ppm.

Anal. Calcd for $C_4H_7Br_2O_2P$: C, 17.29; H, 2.54; Br, 57.51; P, 11.15; MW, 277.9. Found: C, 17.16; H, 2.46; Br, 57.85; P, 11.16; MW (by titration), 277.5.

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REFERENCES

1. K. Moedritzer, *Synth. React. Inorg. Met.-Org. Chem.*, **5**, 45 (1975).
2. J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry*, W. A. Benjamin, Inc., New York, N.Y., 1965, pp. 175.
3. K. Moedritzer, *Z. Anorg. Allg. Chem.*, **458**, 183 (1979).
4. B. Ray Stults and K. Moedritzer, *Cryst. Struct. Comm.*, **8**, 767 (1979).
5. E. Alver and H. M. Kjøge, *Acta Chem. Scand.*, **23**, 1101 (1979).
6. V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Topics in Phosphorus Chemistry*, **5**, 227 (1967).
7. L. C. Thomas, *Interpretation of the Infrared Spectra of Organophosphorus Compounds*, Heyden and Sons Ltd., (1974).
8. P. Haake and P. S. Ossip, *Tetrahedron*, **24**, 565 (1968).
9. W. R. Griffiths and J. C. Tebby, *Phos. and Sulf.*, **5**, 110 (1978).