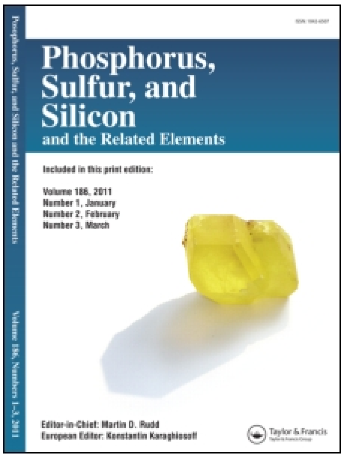

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ORGANOSULPHUR PHOSPHORUS ACID COMPOUNDS. PART 2. ETHANE-1-PHOSPHONO-2-SULPHONIC ACID

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To cite this Article Montoneri, E. and Ricca, G.(1991) 'ORGANOSULPHUR PHOSPHORUS ACID COMPOUNDS. PART 2. ETHANE-1-PHOSPHONO-2-SULPHONIC ACID', Phosphorus, Sulfur, and Silicon and the Related Elements, 55: 1, 111 — 115

To link to this Article: DOI: 10.1080/10426509108045929

URL: http://dx.doi.org/10.1080/10426509108045929

Phosphorus, Sulfur, and Silicon, 1991, Vol. 55, pp. 111–115
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ORGANOSULPHUR PHOSPHORUS ACID COMPOUNDS. PART 2. ETHANE-1-PHOSPHONO-2-SULPHONIC ACID

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(Received March 3, 1990; in final form May 14, 1990)

A new organosulphur phosphorus compounds, ethane-1-phosphono-2-sulphonic acid, has been obtained by phosphonation and sulphonation of 1,2-dibromoethane. The ^{1}H-nmr spectra in D_2O show that the title compound lies mainly in the trans conformation up to 130°C.

Key words: Ethane-1-phosphono-2-sulphonic acid; phosphonation; sulphonation; isomers; ^{1}H-nmr; rotation; hindrance.

Alkanephosphonic-sulphonic acids, $H_2O_3P(CH_2)_nSO_3H$ (I), are not well known. Yet, these compounds are desirable intermediates for the synthesis of new organo-inorganic materials, such as the phosphonates of tetravalent metals with acid groups of variable strength.[1]

To the extent of our knowledge, propane-1-phosphono-3-sulphonic acid[2] is the only compound which has been reported so far to have structure I. This acid has been obtained from sodium diethylphosphite and propane sultone and has been used in the preparation of the zirconium salt without prior structural characterization.

This work on ethane-1-phosphono-2-sulphonic acid discloses a different approach to synthesis of compounds I, starting from 0,0-diethyl-2-bromoethyl phosphonate or from 1,2-dibromoethane. The title compound also offered scope to assess the effect of the two bulky strongly polar acid substituents on the rotational isomerism[3] about the sp^3-sp^3 C—C bond.

RESULTS AND DISCUSSION

The title compound, identified as reported in the Experimental part, has been obtained through the following reactions:

$$\mathrm{Br(CH_2)_2Br + P(OEt)_3 \longrightarrow \underset{(II)}{Br(CH_2)_2PO_3Et_2} + EtBr} \qquad (1)$$

$$\mathrm{II} + \mathrm{Na_2SO_3} \longrightarrow \underset{\text{(III)}}{\mathrm{NaO_3S(CH_2)_2PO_3Et_2}} + \mathrm{NaBr} \tag{2}$$

$$\mathrm{III} \xrightarrow[-\mathrm{NaCl},\ -2\,\mathrm{EtCl}]{+3\mathrm{HCl}} \underset{\text{(IV)}}{\mathrm{HO_3SCH_2CH_2PO_3H_2}} \tag{3}$$

Reaction (1) is known[4] for not being selective, leading to a mixture of II, of 0,0-diethyl-ethyl phosphonate (V) and of ethane-1,2-tetraethyldiphosphonate (VI) because of side reactions.

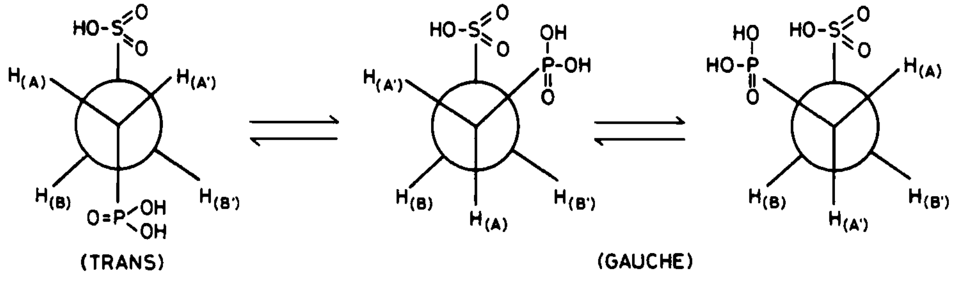
$$\mathrm{P(OEt)_3} \longrightarrow \underset{\text{(V)}}{\mathrm{EtPO_3Et_2}} \tag{4}$$

$$\mathrm{II} + \mathrm{P(OEt)_3} \longrightarrow \underset{\text{(VI)}}{\mathrm{Et_2O_3P(CH_2)_2PO_3Et_2}} + \mathrm{EtBr.} \tag{5}$$

When carried on through the whole reaction scheme (1–3), V and VI hydrolyze, as well as III, and yield a mixture of free acids, posing the problem of isolating IV.

For the purpose of this work, we have considered two alternative procedures: (i) to use in reactions (2) and (3) the pure compound (II), separated from the by-products (V and VI) by distillation[4] or (ii) to use the crude product of reaction (1) and isolate IV from the end product mixture. Both procedures have given satisfactory results. The pure acid (IV) has been obtained by reacting pure II, as in Equation 2 and 3. Alternatively, when crude II was used in reactions (2) and (3), pure IV was isolated by selective precipitation of the barium salt from the end product mixture and followed by ion exchange (see Experimental). This latter finding, in conjunction with previous work on benzenephosphono-3-sulphonic acid[1] and benzenephosphono-3,5-disulphonic acid,[5] seems to indicate that barium ions may be used to isolate either aliphatic and aromatic phosphono-sulphonic acids from their reaction mixtures, since barium phosphonates[6] and barium sulphonates[7] are more water soluble and are better precipitated from water-ethanol mixtures. The solubility property of the barium salt of compound IV thus allows to carry out reactions (1–3), starting from the dihalogeno compound, without isolation of the halogenoalkyl phosphonate intermediate. This procedure would be even more advantageous for the synthesis of high molecular weight alkanephosphono-sulphonic acids, where distillation of the high boiling bromoalkylphosphonate is impractical.[6]

Due to the nature of the substituents, the study of the rotational isomerism about the C—C in IV is of particular interest. For the equilibrium conformations



(TRANS) (GAUCHE)

it was expected that possible intramolecular H-bonding, or protonation interaction, between the acid functional groups could favor a gauche isomer. However, if steric repulsion between the substituents prevailed, the trans conformer had to be preferred.

The ^{31}P-decoupled ^{1}H-nmr spectrum (Figure 1) was fully analyzed as an AA'BB'-type spin-system. Spectral pattern refinement, which was performed using the Bruker Panic Program, produced the following values for the chemical shifts (δ, ppm) and for the coupling constants[8] (J, Hz): $\delta_{H(A)} = \delta_{H(A')} = 2.1$, $\delta_{H(B)} = \delta_{H(B')} = 3.0$ (relative assignment made on obvious shielding effect considerations); $J_{AA'} = -12$, $J_{AB} = J_{A'B'} = 3.5$, $J_{AB'} = J_{A'B} = 14.4$, $J_{BB'} = -13$. The ^{31}P-undecoupled ^{1}H-nmr spectrum (Figure 2) was then analyzed using these spectral parameters and identifying the following $^{2}J_{H\text{-}P}$ and $^{3}J_{H\text{-}P}$ constants by homonuclear ^{1}H double resonance experiments: $J_{H(A)P} = 22.0$, $J_{H(A')P} = 18.5$, $J_{H(B)P} = 11.0$, $J_{H(B')P} = 8.5$ Hz. The high experimental vicinal coupling $J_{AB'} = J_{A'B} = >10$ Hz is unambiguously consistent[9] with a trans arrangement of the involved nuclei. A 100% population of this rotational isomer can be therefore deduced for ethane-1-phosphono-2-sulphonic acid in the solution state. Raising the temperature up to 130°C did not change the spectral pattern, revealing hindered rotation about the C—C bond up to this temperature.

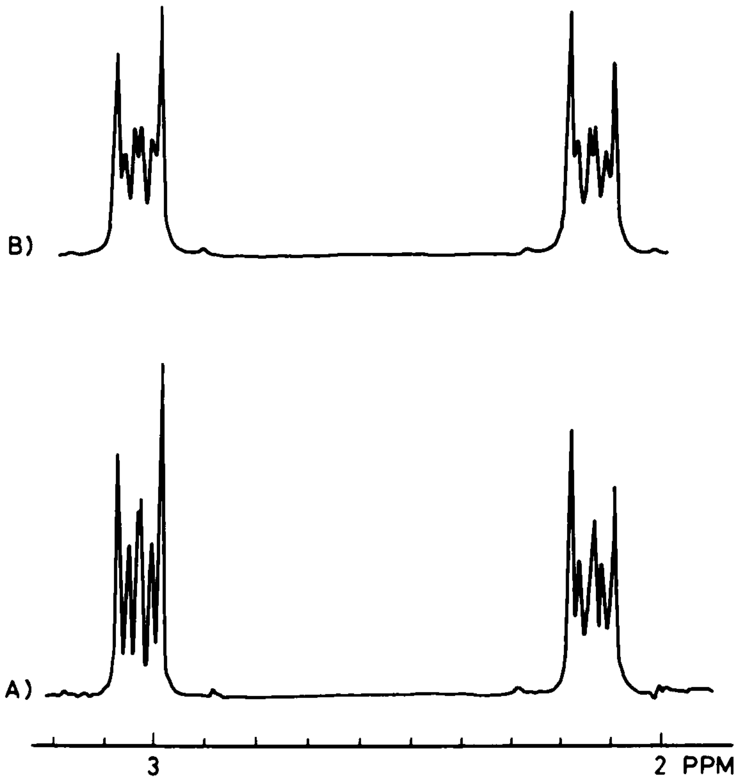


FIGURE 1 Calculated (B) and experimental (A) 200 Mhz ^{31}P-decoupled ^{1}H-nmr spectra of ethane-1-phosphono-2-sulphonic acid in D_2O at 25°C.

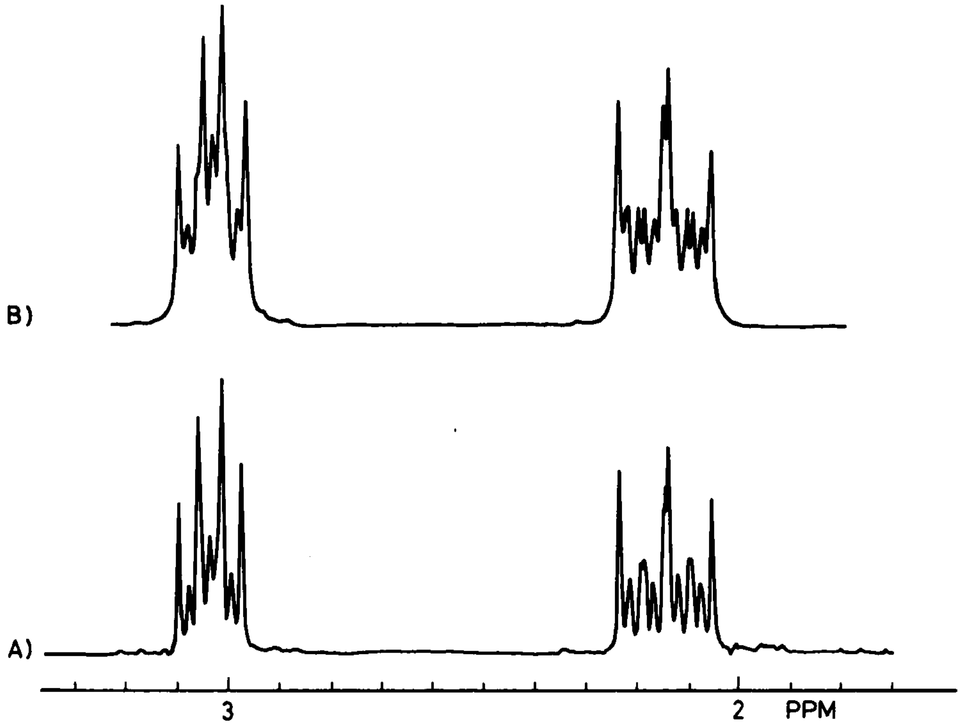


FIGURE 2 Calculated (B) and experimental (A) 200 Mhz ^{1}H-nmr spectra of ethane-1-phosphono-2-sulphonic acid in D_2O at 25°C.

EXPERIMENTAL

Reagents. Triethyl phosphite (TEP) and 1,2 dibromoethane were purchased from Fluka. 0,0-Diethyl-2-bromoethyl phosphonate was purchased from Aldrich. The other reagents were C. Erba RPE products. All materials were used without any further purification.

Physical Measurements. TGA-DTA scans were performed in a Mettler TA 2000 C instrument, in 100 mL/min N_2, from ambient to 200°C at 10°C/min. Infrared spectra (KBr pellets) were recorded on Perkin Elmer 752 spectrometer. ^{1}H (at 200 MHz), ^{13}C (at 50.288 MHz) and ^{31}P (at 80.961 MHz) nmr spectra were recorded on XL 200 Varian spectrometer in D_2O solution containing 15% w/w of IV. Chemical shifts (δ) are in ppm, relative to internal TMS for ^{1}H and ^{13}C and to external 85% H_3PO_4 for ^{31}P; coupling constants (J) are in Hz.

Preparation and Isolation of IV from 1,2-dibromoethane. 1,2-dibromoethane was caused to react with $P(OEt)_3$ as previously reported[4] to yield crude 0,0-diethyl-2-bromoethylphosphonate (EBDP). The product (16.6 g), free of unreacted 1,2-dibromoethane (removed by vacuum distillation), was added to a boiling solution containing 11.5 g anhydrous sodium sulphite in 35 mL water, over a period of 20 minutes and under nitrogen. Upon cooling, the solution was percolated through Dowex 50 W-X8, H^+ form resin (purchased from Baker Chemical Co), until sodium free. The eluate was evaporated in a rotary vacuum evaporator to yield 22.8 g of a liquid residue (A). The residue (A) was taken up in 100 mL concentrated HCl, refluxed for 20 h and evaporated as above to yield a viscous liquid residue (B). The residue (B) was dissolved in 200 mL H_2O, boiled and $Ba(OH)_2$ was added to pH ~ 5. A precipitate was thus obtained. This was filtered to yield a solid product (C) and the solution (D). The solid (C) was taken up in water and HCl was added to it until it dissolved; it was then percolated through the above resin until barium free, evaporated as usual and, then, further dried at 90°C/1 mm Hg for 8 h. The final product (4 g) was identified as ethane-1-phosphono-2-sulphonic acid (IV), containing 10.1% water, from the elemental analysis (found: C 11.3, H 4.5, S 15.2, P 14.5% w/w; theor. for the anhydrous product: C 12.6, H 3.7, S 16.9, P 16.3% w/w), from its neutral equivalents (found by alkali titration to phenolphtalein end point: 14.0 meq H^+/g; theor. for the anhydrous product: 15.8 meq H^+/g) and from the nmr spectra in D_2O: $\delta_{H(A),H(A')} = 2.1$ ppm and $\delta_{H(B),H(B')} = 3.0$ ppm, both multiplets in 1:1 signals area ratio; $\delta_{31\text{-}P} = 26.5$ ppm, proton-decoupled singlet; $\delta_{13\text{-}C} = 49.1$ ppm, singlet, S-bonded C and $\delta_{13\text{-}C} = 25.9$ ppm, doublet, P-bonded C, $J_{C\text{-}P} = 133.2$ Hz, in the proton-decoupled spectrum. DTA-TGA scanning showed that the product melts at 156°C and is stable up to 200°C. The Ir spectrum of the product exhibited the characteristic bands of hydrated $\text{-SO}_3\text{H}$ and $\text{-PO}_3\text{H}_2$ functional groups; a very broad strong band covering the 3600–2000 cm^{-1} range and showing three absorption maxima at ca. 3600, 2840 and 2300 cm^{-1} (H-bonded O—H stretching), a broad medium intensity band at 1625 cm^{-1} (O—H bending), very strong bands at 1275, 1200, 1145, 1035, 960, 920 and 750 cm^{-1}, strong bands at 750, 530, 490 and 445 cm^{-1}, medium intensity bands at 1425, 1110, 610 and 602 cm^{-1} and weak bands at 1330 and 800 cm^{-1}. SO and PO absorptions are both expected in the spectral region below 1450 cm^{-1}. However, no assignment is given here since the spectrum was not well resolved. By comparison, the Ir spectrum of the solid C was much less broad; three weak bands, with much better defined maxima, at 3620, 2920 and 2300 cm^{-1}, indicated that this product was an acid salt,(1) presumably $(\text{O}_3\text{SCH}_2\text{CH}_2\text{PO}_3\text{H})\text{Ba}$. No further structural studies were carried out on the solid (C).

The above solution (D) was added to excess ethanol and a precipitate (E) was obtained which, after filtration, was worked up, as the solid (C), to yield 6.5 g of a product (F). This last product was estimated to contain no more than 25% of ethane-1-phosphono-2-sulphonic acid from its total sulphur content (S% w/w = 4.5). Further fractionation of this product was not attempted.

Preparation of IV from commercial 0,0-diethyl-2-bromoethylphosphonate (97% purity, purchased from Aldrich). This reagent was reacted as the crude product (EBDP) obtained above to yield 4.0 g of IV.

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