Table I

Alcohol	Product	% yield
$C_6H_5CH_2OH$	C_6H_5CHO	84
p-$CH_3OC_6H_4CH_2OH$	p-$CH_3OC_6H_4CHO$	87
$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	80
dl-Menthol	*dl*-Menthone	85
Cyclohexylcarbinol	Cyclohexylcarboxaldehyde	80
$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CHO$	82
$C_6F_5CH_2CH_2OH$	$C_6F_5CH_2CHO$	90
p-$ClC_6H_4CH_2CH_2OH$	p-$ClC_6H_4CH_2CHO$	80
p-$CH_3OC_6H_4CH_2CH_2OH$	p-$CH_3OC_6H_4CH_2CHO$	81
$C_6H_5CH_2CH_2CH_2OH$	$C_6H_5CH_2CH_2CHO$	80
$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCHO$	85
$C_6H_5CHOHCH_3$	$C_6H_5COCH_3$	85
$C_6H_5CHOHC_6H_5$	$C_6H_5COC_6H_5$	85
p-$ClC_6H_4CHOHC_6H_5$	p-$ClC_6H_4COC_6H_5$	84
Cyclohexanol	Cyclohexanone	89

70° by occasional cooling. The mixture was heated at 70° for an additional 30 min, when it became dark green. It was poured on ice and extracted three times with 100 ml each of ether; the combined ether extract was washed once with sodium bicarbonate solution and once with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the remaining oil distilled to give 4.5 g of benzaldehyde (bp 179°), 2,4-dinitrophenylhydrazone mp 237°.

This method with a slight modification is applicable to the preparation of arylacetaldehydes from 2-arylethanols which, when oxidized with ceric ammonium nitrate, give substituted benzaldehydes.[16] Similarly, 3-phenyl-1-propanol, 1-phenylethanol, and cinnamyl alcohol were oxidized to the corresponding carbonyl compounds in 80–85% yields. Table I contains a number of alcohols which were oxidized. All the carbonyl compounds were characterized by their boiling points (or melting points) and 2,4-dinitrophenylhydrazones.

It may be pointed out that DMSO-CrO_3 and DMSO-$K_2Cr_2O_7$ systems also worked in the case of benzyl alcohol. The scope of these oxidation methods to various alcohol systems is currently under investigation and will be reported later.

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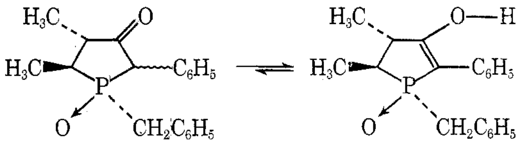
Single-Crystal Analysis of 1-Benzyl-2-phenyl-4,5-dimethylphospholan-3-one 1-Oxide. Evidence for the Enol Form 1-Benzyl-2-phenyl-3-hydroxy-4,5-dimethylphosphol-2-ene 1-Oxide

Summary: An X-ray diffraction analysis of the title compound clearly indicates the existence of the enol form and the stereochemistry at P→O and CH_3 at C(5) to be cis and the CH_3 groups at C(5) and C(4) to be trans.

Sir: In a recent pmr and ^{31}Pmr study[1] of several substituted phospholan-3-one 1-oxides, it was strongly suggested that the oxide 1 existed to a considerable extent in the enol form 2 in $DCCl_3$ and had the stereochemistry as illustrated.



1 2

Molecular models also favored the cis relationship of P→O and CH_3 at C(5) and trans relationship of the two CH_3 groups.[2-4] We wish to report the first single-crystal analysis of the enol title compound, mp 181–183°.

The space group is orthorhombic $Pc2_1b$ (no. 29) with unit cell dimensions of $a = 8.1319$ (6), $b = 8.5671$ (7), and $c = 24.081$ (3) Å for $C_{19}H_{21}O_2P$. The integrated intensities of 1852 independent reflections were taken on a CAD-4 automatic diffractometer, using CuKα ($\lambda = 1.5418$) radiation. This constitutes all the independent data with $\theta \leq 75°$. The structure was solved from a Patterson synthesis and the heavy atom method, and was refined by block-diagonal least-square methods. The final R value $[R = (\Sigma||F_o| - |F_c||)/\Sigma F_o$ is 0.035.

Bond lengths and angles are given in Figure 1. The standard deviations of the P–C distances are between 0.002 and 0.003 Å. The standard deviations of the C–C distances are between 0.003 and 0.005 Å. All other results are on the figure. Figure 2 is a 3-D representation of the molecule.

First, it is apparent that the C(2)–C(3) bond is quite near that of an alkene linkage in length and that 2 is the tautomer in the solid state. Strong intermolecular H bonding is evidenced by an O–O distance of 2.593 Å between two molecules. Thus, it is strongly suggested that C(2) and C(3) are very close to sp^2 hybridized. This can be deduced from the observation that the sum of the three bond angles around the atoms is 360.0 and 359.9°, respectively. There is, however, a small rotation around the C(2)–C(3) bond as indicated by the conformational angle of 8° for the atoms PC(2)C(3)C(4). This probably is correlated with the obser-

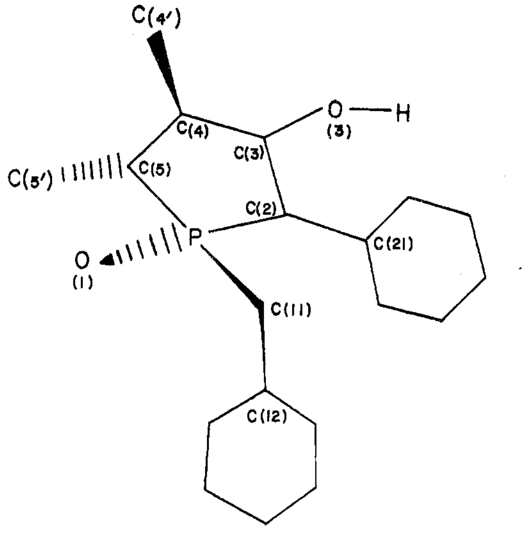


Figure 1. Molecular structure of 1-benzyl-2-phenyl-3-hydroxy-4,5-dimethylphosphol-2-ene 1-oxide (**2**). Molecular dimensions are P–C(2) = 1.776, P–C(5) = 1.822, P–C(11) = 1.819, P–O(1) = 1.506, C(11)–C(12) = 1.521, C(2)–C(3) = 1.356, C(2)–C(21) = 1.477, C(3)–C(4) = 1.505, C(3)–O(3) = 1.337, C(4)–C(5) = 1.551, C(4)–C(4′) = 1.534, C(5)–C(5′) = 1.530, mean phenyl C–C for C(12) ring = 1.381, mean phenyl C–C for C(21) ring = 1.385 Å; angles are PC(2)C(3) = 108.2, PC(2)C(21) = 123.7, C(3)C(2)C(21) = 128.1, C(2)C(3)C(4) = 118.9, C(2)C(3)O(3) = 122.8, C(4)C(3)O(3) = 118.2°.

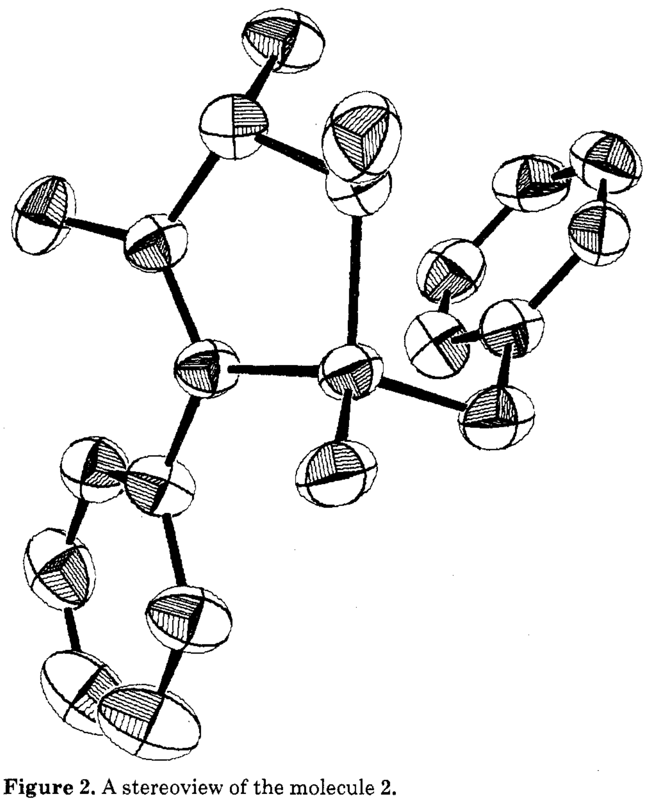
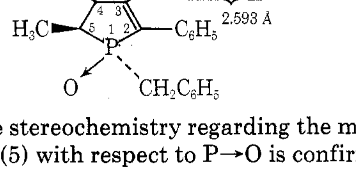
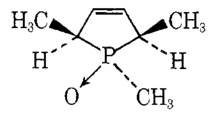


Figure 2. A stereoview of the molecule **2**.

vation that the C(2)–C(3) distance (1.357 Å) appears to be slightly longer than a pure alkene bond.



Second, the stereochemistry regarding the methyl groups at C(4) and C(5) with respect to P→O is confirmed as trans and cis, respectively. Thus, coupling of J_{PCH} = 7 Hz [P→O and H(5) are trans] is in good agreement with the J_{PCH} = 6.50 Hz for **3**.[5] On the basis of our stereochemical data



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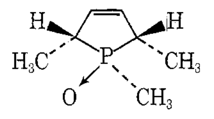

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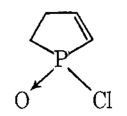
[around C(4), C(5), and P→O] for **2**, support is also advanced for the argument[5b] that the CH_3 group is trans to the P→O function in **4** which has a ^{13}C resonance more deshielded than in the cis arrangement in **3**.

To our knowledge, this structural study is the first recorded on a 3-hydroxyphosphol-2-ene system. Comparison of the dimensions in **2** with those in 1-chlorophosphol-2-ene 1-oxide (**5**)[6] and 1-benzylphosphole (**6**)[7] is instructive.



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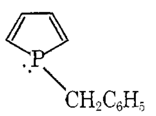

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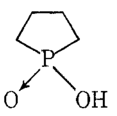

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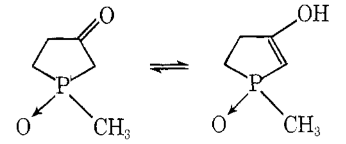
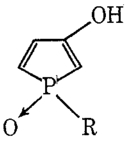
Interestingly, the P–C(sp^2) bond length (1.776 Å) in **2** is only slightly shorter than the counterpart in **5** (1.791 Å)[6] and in **6** (1.783 Å, average value).[7] In contrast, the P–C(sp^3) bond length (1.822 Å) is longer in **2** than in **5** (1.791 Å) and in 1-hydroxyphospholane 1-oxide (**7**) (1.786 Å, average value).[8] In our opinion, the role of d orbitals on phosphorus in the C–P bonding of these systems is poorly understood. Consequently, speculation as to the magnitude of electronic effects of alkyl, hydroxy, or halogen groups attached to P on a geminal P–C(sp^2) or P–C(sp^3) bond length must await more quantitative data on the bonding properties.

Recent chemical and spectral evidence indicates high enolic content of **8**.[9] A search of the literature revealed no



8

other examples of the family or of the closely related family, 1-substituted 3-hydroxyphosphole 1-oxides (**9**). Though no information could be found on the somewhat analogous sulfoxide or sulfone, the data on highly unstable **10** suggest



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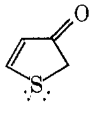

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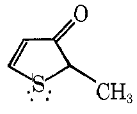

11

an approximate 1:1 ratio of keto and the enol tautomer by ir (liquid film) studies.[10] Pmr analysis of relatively stable **11** gave a 1:4 ratio of **11** to its enol form.[11] Quite probably, stabilization of the C=C–C=O system increases the propensity for generation of the suspected less stable keto form in solution. Unfortunately, no X-ray analysis of any member of these families could be uncovered. The rarity of the 2-phospholen-3-ole structure and the fact the O- and C-alkylation appears to be sterically influenced[1] should stimulate interest in the family as starting materials for C–P heterocycles with possible biological activity.[12]

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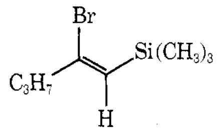
Addition of Hydrogen Bromide to 1-Trimethylsilyl-1-alkynes. A Convenient Synthesis of 2-Bromo-1-alkenes

Summary: The reaction of anhydrous HBr with terminal trimethylsilylalkynes is a rapid free-radical reaction resulting in the elimination of the trimethylsilyl group as the halide and the production of 2-bromo-1-alkenes in high yield; a series of alkynes were studied and some mechanistic details elucidated; the method represents a significant improvement in the synthesis of 2-bromo-1-olefins over existing literature methods.

Sir: For the purposes of other synthetic work, we required a method for the preparation of several isomeric substituted bromovinylsilanes (*e.g.*, β-bromo isomer 1). One approach to the synthesis of 1 was the addition of hydrogen bromide to 2 in the presence of free-radical initiators like benzoyl peroxide. Previous workers had documented the free-radical addition of hydrogen bromide to trimethylsilylacetylene itself.[1] However, upon exposure of 2, prepared from lithio-1-pentyne[2] and trimethylsilyl chloride, to excess anhydrous hydrogen bromide under conditions similar to those previously used, no products of the volatility expected for 1 were isolated. On closer examination, the major product was identified as 2-bromo-1-pentene (3).[3] This curious result led us to investigate this process further.



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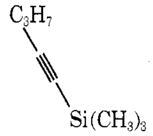

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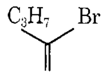

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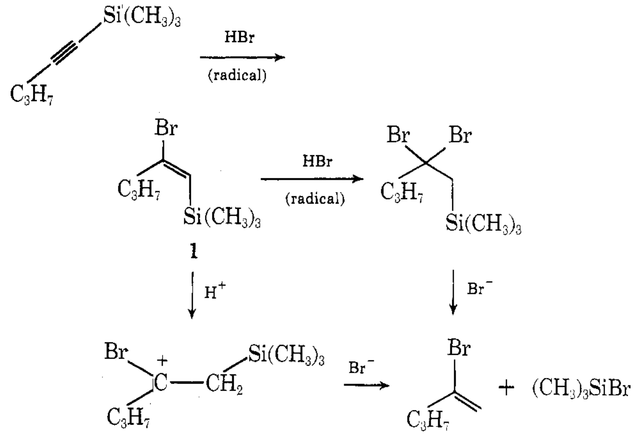
Addition of hydrogen bromide to terminal acetylenes is known to produce exclusively 1-bromo-1-alkenes, along with varying amounts of 1,2-dibrominated material.[4] Ionic addition, while extremely sluggish, leads to the 2-bromo isomer in poor yield as well as other dibrominated materials.[5] The apparent rapidity of the reaction with 2 suggested that a radical mechanism was involved.

When the total reaction mixture was examined, another substance produced in about the same amount as the bromo olefin was isolated and identified as trimethylsilyl bromide. We were led to postulate the mechanism shown in Scheme I. The first step of this mechanism is supported by the following data: (1) no addition occurs with anhydrous hydrogen chloride;[6] (2) addition of 2,6-di-*tert*-butyl-4-methylphenol (BHT), a known radical inhibitor, results in complete inhibition of the reaction with hydrogen bromide; (3) under carefully controlled conditions up to 60% of the mono addition product (1) can be isolated; (4) as mentioned above the expected stoichiometric quantities of trimethylsilyl bromide were isolated.

Scheme I



There are two likely mechanistic pathways for the second (and succeeding) step(s) from bromovinylsilane (1), ionic or radical as shown. We have established that 1 is transformed by hydrogen bromide to 2-bromoolefin with high efficiency. Our efforts to inhibit this very rapid conversion have been unsuccessful. However, the transformation does not occur upon treatment with anhydrous hydrogen chloride contrary to expectation if the reaction were proceeding by an ionic pathway. While we cannot absolutely rule out an ionic pathway, the radical pathway seems most likely. The final β elimination of trimethylsilyl halides is well documented[7] and has been used recently in a synthesis of 1-bromo olefins.[8] Although β eliminations of this type usually proceed *via* an ionic pathway, there is no evidence to preclude a radical or thermal pathway.[7]

Since a search of the literature led us to the conclusion that few viable synthetic routes to functionalized 2-bromo-1-alkenes exist,[5,9] we subjected a representative series of trialkylsilylacetylenes to anhydrous acid treatment as previously described. The results may be found in Table I.

It was found on a preparative scale that reactions may be run neat at 0° if the acetylene is a liquid, in solvents such as pentane and hexane (reaction rate is reduced), and in