Alkaline Hydrolysis of 1-Iodomethyl-1,2,5-triphenylphospholium Iodide, a New Route to the 4-Phosphabicyclo[3.1.0]hex-2-ene System

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Alkaline hydrolysis of 1-iodomethyl-1,2,5-triphenylphospholium iodide gives 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide in very high yield. Three possible mechanisms are discussed and isolation of a key intermediate allows one of these mechanisms to be discarded. Alkaline hydrolysis of 1-allyl-1,2,5-triphenylphospholium bromide in methanol gives 1,2,5-triphenylphosphole and small quantities of a compound $C_{26}H_{27}O_2P$ which is an adduct of the original phospholium ion, hydroxide ion, and methanol.

L'hydrolyse alcaline de l'iodure de l'iodométhyl-1 triphényl-1,2,5 phospholium donne le triphényl-3,4,5 phospha-4 bicyclo[3.1.0]hexène-2 oxyde-4 avec un excellent rendement. Trois mécanismes possibles sont discutés; un de ceux-ci peut toutefois être rejeté en se basant sur le fait qu'un intermédiaire important a pu être isolé. L'hydrolyse alcaline du bromure d'allyl-1 triphényl-1,2,5 phospholium dans le méthanol donne le triphényl-1,2,5 phosphole et de petites quantités d'un composé en $C_{26}H_{27}O_2P$ qui est un produit d'addition de l'ion phospholium original avec l'ion hydroxyle et le méthanol.

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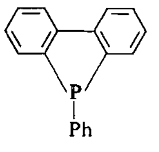
Ring expansion reactions of the phosphole system have been comparatively little explored as possible routes to six-membered unsaturated phosphorus heterocycles (1–4). One approach, due to Millar (3), involves the reaction of 9-phenyl-9-phosphafluorene (the dibenzophosphole **1**) with methylene iodide to give the salt **2** which on treatment with hydroxide ion gives **3** (in very good yield) by cleavage of the phosphole ring in the manner observed by Bergesen (5) followed by attack of the resulting carbanion (which migrates from the apical position of a trigonal bipyramidal intermediate (3)) upon the methylene group and displacement of iodide ion. This type of 1,2-migration has been shown to be fairly general in the hydrolysis of suitably substituted phosphonium compounds and similar ring expansions occur in the phosphetan system (6).



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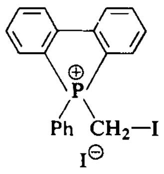

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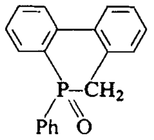

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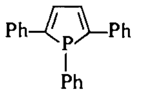

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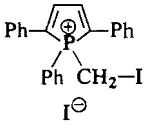
Simple phospholes are now relatively easily available (7) and the above reaction applied to simple phospholes could prove to be a convenient route to phosphorins, particularly those with unsymmetrical substitution patterns. In order to explore this possibility, 1,2,5-triphenylphosphole (**4**) was treated with methylene iodide in a pressure bottle for 4½ days to give an excellent yield of the corresponding phospholium iodide **5**. Alkaline hydrolysis of **5** was expected to give the phosphacyclohexa-2,4-diene **6** since the five-membered ring should occupy an apical–equatorial arrangement in the expected trigonal bipyramidal intermediate (6) but, rather surprisingly, a 74% yield of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (**7**) (identical with an authentic sample (1)) was obtained when **5** was treated with aqueous methanolic sodium hydroxide for 24 h under reflux followed by acidification of the reaction mixture. This bicyclic compound has recently been shown (4) to be of value in the synthesis of six-membered ring phosphorus heterocycles.



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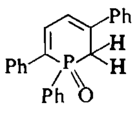

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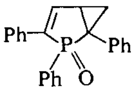

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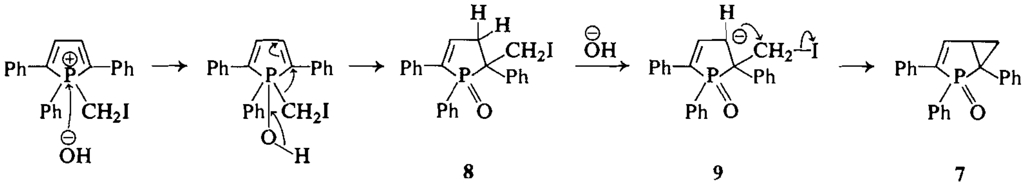
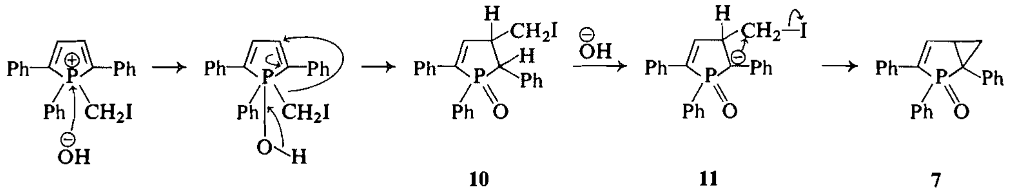
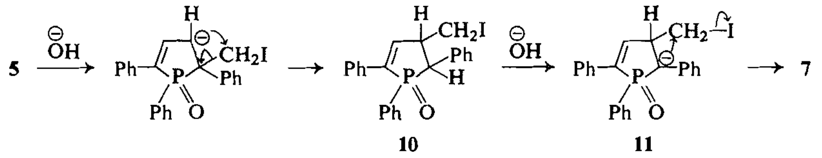


SCHEME 1



SCHEME 2



SCHEME 3

There are several possible mechanisms for the formation of **7** from **5**. At first sight perhaps the most likely of these is a 1,2-migration of the iodomethyl group followed by proton abstraction by hydroxide ion and ring closure involving expulsion of iodide ion as shown in Scheme 1. However, hydroxide ion abstraction of the allylic protons would seem unlikely. This reaction would parallel the 1,2-migrations observed (6) in other phosphonium salt hydrolyses but it would imply that, in this case, the five-membered ring does not occupy an apical–equatorial arrangement in the intermediate or that in the case of **2**, a —CH_2I migration of the type outlined in Scheme 1 is inhibited by the fused nature of the ring system.

A second possible mechanism is illustrated in Scheme 2. In this case a 1,3-migration of the iodomethyl group occurs and the intermediate carbanion **11** could be to some extent stabilized by overlap with the d-orbitals of the neighboring phosphorus atom. However, this would be a most unusual type of rearrangement which would be difficult to account for except that it involves attack at the β-position of a vinylphosphonium type of system.

A third possibility[1] (Scheme 3) is that the intermediate **10** is formed by two consecutive 1,2-shifts of the iodomethyl group rather than a single 1,3-shift. The driving force for the second of these migrations would presumably come from the conversion of an allylic carbanion type of intermediate into the protonated α-phosphoryl benzylic carbanion **10**.

If any of these reaction schemes operates and if the predicted intermediate **8** or **10** has a significant lifetime it could possibly be isolated. Therefore, in an attempt to isolate the predicted intermediate, the reaction was carried out under much milder conditions at room temperature for 2 h. The product (obtained in good yield) was not **7** but analyzed well for $C_{23}H_{20}OPI$ and the mass spectrum confirmed the molecular weight as 470. The i.r. spectrum shows a typical P=O stretching vibration at 1180 cm^{-1} and the u.v. spectrum (ethanol) shows λ_{max}(log ε) at 220 (4.33) and 261 mμ (4.07), indicating considerable loss of conjugation relative to **5**. The n.m.r. spectrum shows a ratio of 16 aromatic and olefinic protons

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[1] We are indebted to one of the referees for this suggestion.

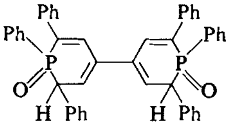
(complex multiplet at τ 2.19–3.16) to two methylene or methine protons (multiplet at τ 5.52–6.08) to two methylene protons (multiplet at τ 6.65–7.02). That the compound is not a mixture of **8** and **10** was shown by a detailed t.l.c. examination on both alumina and silica of various activities using several solvent systems.

In our opinion, this evidence fits structure **10** considerably better than it fits structure **8**. Thus, structure **8** contains two allylic methylene protons which could possibly account for the multiplet in the n.m.r. spectrum at τ 6.65–7.02, although a signal at somewhat higher field would be expected. However, this would mean that the methylene protons of the iodomethyl group would be responsible for the signal at τ 5.52–6.08 which is clearly at too low field for such protons even bearing in mind the probable deshielding effect of the P=O grouping. Indeed, even in **5**, where the deshielding effect of the neighboring phosphonium grouping (8) is at a maximum, the methylene protons appear only as low as τ 5.68.

Equally, if the n.m.r. signal assignments for **8** are reversed, the signal at τ 6.65–7.02 would agree well with that expected for the methylene protons of the iodomethyl group (*cf.* ethyl iodide (9)) but the signal at τ 5.52–6.08 is again at too low field for the allylic methylene group which is relatively remote from the P=O grouping and attached to only a mildly electron-withdrawing group. Such a signal would be unlikely to occur below τ 7 unless some additional strong deshielding effect were present. For example, even in allyl bromide, where deshielding is very strong, the allylic methylene protons still resonate at τ 6.07 (10). The additional deshielding effect could conceivably be provided by the neighboring phenyl group but, if this were the case, it seems unlikely that both of the non-equivalent protons would be deshielded to the same extent bearing in mind the probable stereochemistry of the system.

On the other hand, in structure **10**, the signal at τ 6.65–7.02 agrees well with that expected for the iodomethyl group as in ethyl iodide (9) and the signal at τ 5.52–6.08 could be generated by the two tertiary protons both of which are allylic (or benzylic) and adjacent to electron-withdrawing groups. Furthermore, the benzylic protons in **12** have been shown to resonate in the same region at τ 6.11 (4).

It is worth noting that the side-chain methylene group of **10** appears as a multiplet of at least five peaks rather than a doublet in the n.m.r. spectrum. This is almost certainly because the two methylene protons are non-equivalent due to the adjacent asymmetric center since long-range coupling with the phosphorus atom would be very small. Such a case is similar to that of the diastereomeric methylene protons of 1,2-dichloropropane (11). The methine protons appear as a multiplet because of coupling with each other, the non-equivalent methylene protons and the phosphorus atom. In structure **8**, the protons in both methylene groups would be non-equivalent due to the neighboring asymmetric center so that the multiplicities of the signals are of little value in distinguishing between **8** and **10**. Also, the fact that both **8** and **10** could be mixtures of the various possible stereoisomers cannot be ignored.

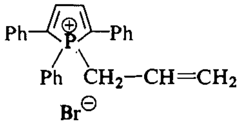


12

Further treatment of **10** with sodium hydroxide in aqueous methanol under reflux for 24 h gives an almost quantitative yield of the cyclopropane **7**. This supports our tentative conclusion that **10** (and not **8**) is the intermediate isolated since it is unlikely that the protons of the allylic methylene group in **8** would be sufficiently acidic to be abstracted by hydroxide ion whereas benzylic protons of the type present in **10** and **12** are known to be abstractable by strong base (4). The compound assumed to be **10** is also converted very rapidly into **7** on treatment with sodium hydride in rigorously dried (molecular sieves) dimethylformamide. This, then, strongly suggests that **10** is formed as an intermediate in the alkaline hydrolysis of **5** and that the reaction proceeds via Schemes 2 or 3. Attempts to reduce the side-chain iodomethyl group of **10** with lithium aluminum hydride gave only resinous materials.

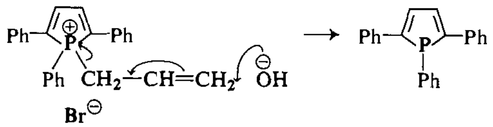
In a final attempt to confirm the identity of **10**, deuterium exchange studies were undertaken. Thus, it was observed that a solution of the compound assigned structure **10** in perdeuteroacetone containing NaOD and D_2O showed no exchange (n.m.r. studies) at room temperature over a period of 2 days. Treatment of the same compound in rigorously dried (molecular sieves) dimethylsulfoxide with NaOD and D_2O resulted in the formation of **7**. The reaction was complete in little over a minute and n.m.r. measurements showed no incorporation of deuterium into the product. A solution of the compound assigned structure **10** in perdeuteroacetone containing NaOD and D_2O was heated under reflux until about 75% conversion into **7** had occurred (approximately 30 min). The n.m.r. studies of the mixture of the product and starting material showed that no deuterium exchange had occurred in the starting material (the peaks at τ 6.65–7.02 and 5.52–6.08 remained of equal area) and that no deuterium had been incorporated into **7**. These studies are inconclusive in that they do not favor either structure **10** or structure **8**. They show only that the proton abstraction steps **8** → **9** (Scheme 1) or **10** → **11** (Schemes 2 and 3) are not reversible under the conditions used and that intramolecular cyclization occurs before reprotonation can occur. However, in our opinion, all the evidence available strongly favors structure **10** in preference to structure **8** for the hydrolysis intermediate $C_{23}H_{20}OPI$.

Similar experiments were carried out with 1-allyl-1,2,5-triphenylphospholium bromide (**13**) in order to see if any corresponding migration of the allyl group occurs.



13

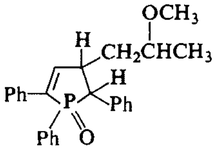
The quaternary salt **13** is readily prepared in very high yield by heating the phosphole **4** with allyl bromide in dry benzene under reflux for several days. Treatment of the quaternary salt with aqueous methanolic sodium hydroxide at room temperature gives at least two products together with large amounts of oily material. The first of these is the phosphole **4**, *not* its oxide as would be expected from normal attack (5) of hydroxide ion at the phosphorus atom, and it therefore appears that attack occurs at the terminal carbon atom of the allyl group with displacement of the neutral phosphole **4** as shown in Scheme 4.



13 **4**

SCHEME 4

The second product, obtained in very small quantities, is a colorless material analyzing for $C_{26}H_{27}O_2P$ and which is therefore an adduct of the phospholium ion **13**, hydroxide ion, and methanol. The mass spectrum confirms the molecular weight as 402 and elemental analyses show the presence of one methoxy group. The u.v. spectrum shows λ_{max}(log ε) at 219.5 (4.27) and 258 mμ (4.01) indicating that the diphenylbutadiene portion of the molecule is no longer intact and that the molecule contains little unsaturation. The i.r. spectrum shows P=O and ether-type C—O stretching vibrations at 1170 and 1105 cm^{-1} respectively. The n.m.r. spectrum shows 16 aromatic and olefinic protons as a complex multiplet at τ 2.15–3.14, three methoxy protons as a sharp singlet at 6.97, five methylene and/or methine protons as a complex multiplet at 5.81–7.99, and three methyl protons as a doublet (J = 6 Hz) at 9.0. Since the methoxy protons appear as a sharp singlet in the n.m.r. spectrum, the methoxy group is not attached to the phosphorus atom because this would give a doublet due to ^{31}P coupling (12).



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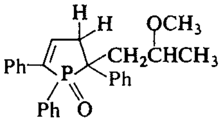

15

It therefore seems likely that migration of the allyl group has occurred and that some kind of addition of methanol to the unsaturated portion of the allyl group has also occurred to give a methyl group adjacent to a tertiary proton. Since only very small quantities of the product were available, the structure determination was not completed. However, structures **14** and **15** are consistent with all the evidence (with **14** preferred by analogy with **10**) but, apart from migration of the allyl group to the 2- or 3-position of the phosphole ring, it is difficult to visualize the reaction sequence which could lead to these structures. Some further evidence for the proposed structures **14** and **15** is given by the u.v. spectrum which is almost identical with that of **10** and by the mass spectrum which shows a very intense peak at m/e 329 corresponding to loss of the allylic or tertiary —$CH_2CH(OMe)CH_3$ group and another strong peak at m/e 328 which suggests that the oxide of the phosphole **4** is regenerated on electron impact. The peak at m/e 329 is also present in the spectrum of the product tentatively assigned structure **10** but is much weaker. This is presumably due to the easy loss of the iodine atom which would lead to a different major fragmentation pattern. The structure of this adduct must, however, remain in doubt pending a complete structure determination.

Experimental

The i.r. spectra were recorded in Nujol mulls using a Beckman IR12 spectrophotometer while u.v. spectra were obtained on dilute ethanol solutions using a Unicam SP800 spectrophotometer. The n.m.r. measurements were made with a Varian Associates model A60-A spectrometer using trifluoroacetic acid or deuteriochloroform solutions with tetramethylsilane as internal reference. Mass spectra were determined using an Hitachi–Perkin–Elmer model RMU-7 double focussing mass spectrometer.

1,2,5-Triphenylphosphole was prepared by the method of Campbell (1).

1-Iodomethyl-1,2,5-triphenylphospholium Iodide (5)

A well-mixed paste of 1,2,5-triphenylphosphole (10 g, 32.05 mmol) and methylene iodide (26 g, 96.95 mmol) in a pressure bottle under dry nitrogen was kept with constant stirring at 80–85° for $4\frac{1}{2}$ days. When cooled, the reaction mixture turned to a dark brown solid which was broken up and washed thoroughly with acetone. The yellow residue (17 g, 91%) was found to be almost pure 1-iodomethyl-1,2,5-triphenylphospholium iodide, m.p. 174–175° (dec.).

Anal Calcd. for $C_{23}H_{19}I_2P$: C, 47.59; H, 3.28; I, 43.79; P, 5.34. Found: C, 47.74; H, 3.45; I, 43.82; P, 5.37.

Attempts to recrystallize the yellow powder from a number of solvents such as benzene, chloroform, acetone, ethanol, methanol, water, acetic acid, dimethylformamide, and mixed solvents were unsuccessful and the material was therefore used directly for further investigation.

The i.r. spectrum of **5** shows ν_{max} at 1579, 1538, 1491, 1472, 1447, 1441, 1384, 1371, 1318, 1302, 1259, 1233, 1168, 1161, 1110, 1080, 1031, 1000, 946, 923, 860, 800, 766, 750, 740, 730, 700, 690 cm^{-1}. The u.v. spectrum in absolute ethanol shows $\lambda_{max}(\log \varepsilon)$ at 225 (4.58), 275 (3.71), and 411 $m\mu$ (4.19). The n.m.r. spectrum in trifluoroacetic acid shows a ratio of 17 aromatic and olefinic protons (complex multiplet at τ 1.75–2.76) to two methylene protons (doublet centered at τ 5.68 with $J_{HP} = 8$ Hz).

Complete Alkaline Hydrolysis of 1-Iodomethyl-1,2,5-triphenylphospholium Iodide (5)

To a suspension of the quaternary salt **5** (8 g, 13.79 mmol) in methanol (800 ml) was added slowly a 10% aqueous solution of sodium hydroxide (55 ml, 137.6 mmol) at room temperature with vigorous stirring. After the addition was complete, the reaction mixture was heated under reflux for 24 h. The cooled solution was then treated dropwise with dilute aqueous hydrochloric acid until it was just acidic to litmus paper. Water (200 ml) was added and the mixture was evaporated under reduced pressure to remove most of the methanol. The aqueous suspension was then extracted with chloroform (3 × 100 ml). The extracts were combined, dried over anhydrous sodium sulfate, reduced to a volume of 50 ml, and chromatographed on a silica gel column using chloroform as the eluent. Evaporation of the eluate to dryness yielded a pale yellow solid which was recrystallized from hot ethanol to give very pale yellow crystals (3.5 g, 74%) of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (7), m.p. 234–235° (dec.), identical in all respects with an authentic sample (1).

Incomplete Alkaline Hydrolysis of 1-Iodomethyl-1,2,5-triphenylphospholium Iodide (5)

To a suspension of the quaternary salt **5** (12 g, 20.68 mmol) in methanol (1200 ml) was added slowly a 10% aqueous solution of sodium hydroxide (83 ml, 207.1 mmol) at room temperature followed by vigorous stirring for 2 h. The solution was then treated dropwise with dilute aqueous hydrochloric acid until it was just acidic to litmus paper. Water (300 ml) was added and the mixture was evaporated under reduced pressure to remove most of the methanol. The aqueous suspension was extracted with chloroform (3 × 50 ml) and the extracts were combined, dried over anhydrous sodium sulfate, and evaporated to dryness. The dark brown residue was dissolved in the minimum amount of benzene and chromatographed on a column of silica gel using successively benzene and chloroform as eluents. The benzene fraction, upon evaporation, yielded a colorless solid which was recrystallized from a hot benzene/cyclohexane mixture to give long colorless needles (5.6 g, 58%) of 4-iodomethyl-1,2,5-triphenyl-2-phospholene-1-oxide (**10**), m.p. 199–200° (dec.).

Anal. Calcd. for $C_{23}H_{20}OPI$: C, 58.71; H, 4.26; I, 27.08; P, 6.60. Found: C, 59.01; H, 4.25; I, 27.09; P, 6.60.

The i.r. spectrum shows ν_{max} at 3058, 1601, 1587, 1499, 1438, 1422, 1304, 1268, 1180, 1159, 1148, 1104, 1068, 1025, 1000, 918, 881, 824, 792, 760, 748, 719, 699, 691 cm^{-1}. The u.v. spectrum in absolute ethanol shows $\lambda_{max}(\log \varepsilon)$ at 220 (4.33) and 261 $m\mu$ (4.07). The n.m.r. spectrum in deuterated chloroform shows a ratio of 16 aromatic and olefinic protons (complex multiplet at τ 2.19–3.16) to two tertiary protons (multiplet at τ 5.52–6.08) to two methylene protons (multiplet of at least five peaks at τ 6.65–7.02). The mass spectrum shows a good molecular ion peak at $m/e = 470$.

The chloroform fraction, upon evaporation to dryness yielded pale yellow crystals of 7 (0.7 g, 10%) identical in all respects with an authentic sample.

Alkaline Hydrolysis of 4-Iodomethyl-1,2,5-triphenyl-2-phospholene-1-oxide (10)

To a solution of the 2-phospholene oxide **10** (1 g, 2.13 mmol) in methanol (100 ml), was added slowly a 10% aqueous solution of sodium hydroxide (8.5 ml, 21.28 mmol) at room temperature with vigorous stirring. After the addition was complete, the mixture was heated under reflux for 24 h. The cooled solution was treated dropwise with dilute hydrochloric acid until it was acidic to litmus paper and the mixture was worked-up and chromatographed in chloroform solution as before. The eluate from the silica column yielded a pale yellow solid which was crystallized from hot ethanol to give very pale yellow crystals (0.65 g, 90%) of the cyclopropane **7** identical in all respects with an authentic sample.

1-Allyl-1,2,5-triphenylphospholium Bromide (13)

The phosphole **4** (15 g, 48.09 mmol) and allyl bromide (29 g, 240 mmol) in dry benzene (500 ml) were heated under reflux in a dry nitrogen atmosphere for 5 days. The yellow solid which separated was collected and recrystallized from hot water or a hot methanol/benzene mixture to give yellow crystals (19 g, 91%) of 1-allyl-1,2,5-triphenylphospholium bromide (**13**), m.p. 202–203° (dec.).

Anal. Calcd. for $C_{25}H_{22}BrP$: C, 69.26; H, 5.07; Br, 18.52; P, 7.15. Found: C, 68.97; H, 5.01; Br, 19.05; P, 7.10.

The i.r. spectrum shows ν_{max} at 3038, 1635, 1610, 1579, 1490, 1443, 1344, 1313, 1259, 1190, 1154, 1108, 1078, 1030, 998, 981, 939, 906, 878, 813, 761, 748, 726, 685 cm^{-1}. The u.v. spectrum in absolute ethanol shows λ_{max} (log ε) at 212 (4.52), 227 (4.58), and 410 mμ (4.12). The n.m.r. spectrum in deuterated chloroform shows a ratio of 20 aromatic and olefinic protons (complex multiplet at τ 1.26–2.96) to two methylene protons (poorly defined quartet centered at τ 5.27).

Alkaline Hydrolysis of 1-Allyl-1,2,5-triphenylphospholium Bromide (13)

A solution of the quaternary salt **13** (1.4 g, 3.24 mmol) in methanol (70 ml) was treated dropwise with a 10% aqueous solution of sodium hydroxide (6.5 ml, 16.25 mmol) at room temperature with constant stirring for 10 min. Water (50 ml) was added and the mixture was evaporated to remove most of the methanol. The aqueous suspension was extracted with chloroform (3 × 50 ml) and the chloroform extracts were combined, dried, and evaporated as before. The residue was chromatographed on a neutral alumina column using successively benzene and chloroform as eluents.

The benzene fraction, upon evaporation to dryness, yielded an oily solid which, on recrystallization from hot ethanol gave the phosphole **4** (0.12 g, 12%) identical with an authentic sample.

Evaporation of the chloroform fraction also yielded an oily solid which was sublimed under vacuum (*ca.* 1 Torr) at 165° to give a colorless compound (0.16 g, 12%), m.p. 171–172°.

Anal. Calcd. for $C_{26}H_{27}O_2P$: C, 77.71; H, 6.72; P, 7.71; OCH_3, 7.71. Found: C, 77.4; H, 6.73; P, 7.60; OCH_3, 6.83.

The i.r. spectrum shows ν_{max} at 3051, 1610, 1600, 1578, 1494, 1431, 1368, 1299, 1262, 1220, 1170, 1105, 996, 955, 920, 878, 826, 791, 774, 752, 743, 718, 688 cm^{-1}. The u.v. spectrum in absolute ethanol shows λ_{max}(log ε) at 219.5 (4.27) and 258 mμ (4.01). The n.m.r. spectrum shows 16 aromatic and olefinic protons as a complex multiplet at τ 2.15–3.14, three methoxy protons as a sharp singlet at 6.97, five methylene and methine protons as a complex multiplet at 5.81–7.99, and three methyl protons as a doublet (J = 6 Hz) at 9.0. The mass spectrum shows a strong molecular ion peak at m/e = 402.

Alkaline hydrolysis using only water as solvent gave a mixture of uncrystallizable oils together with traces of the phosphole **4** and *p*-terphenyl.

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