

REACTION BETWEEN 1,2,5-TRIPHENYLPHOSPHOLE AND DIMETHYL ACETYLENEDICARBOXYLATE

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Abstract—1,2,5-Triphenylphosphole reacts at room temperature with dimethyl acetylenedicarboxylate to give dimethyl 3,6-diphenylphthalate and a yellow 1:2 adduct which is shown by physical and chemical methods to be the 1,1'-spirobiphosphole (VI). Traces of a 1:4 adduct are also formed but the structure of this has not yet been determined.

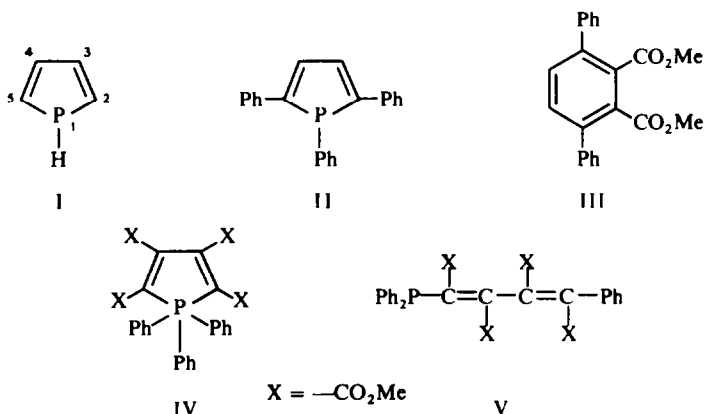
THE phosphole ring system (I) is of interest since it is structurally and electronically similar to pyrrole and is therefore potentially aromatic. However, few simple derivatives of phosphole are known and the evidence for and against aromaticity is conflicting. Thus, it has been concluded¹ that the phosphole ring in 1,2,3,4,5-pentaphenylphosphole has little, if any, aromatic character because of the relative ease with which it forms an oxide and a sulphide and because its reactions with various iron carbonyls suggest that it is a non-aromatic conjugated diene. Also, this phosphole was found to undergo Diels-Alder reactions with maleic anhydride and dimethyl acetylenedicarboxylate although the conditions required (150° in a sealed tube for 15 hr) were considerably more drastic than for many furan derivatives. Other workers have concluded² from chemical evidence that the phosphole ring in 1,2,5-triphenylphosphole (II) also possesses little aromatic character. These observations agree well with theoretical predictions³ and with estimates of the resonance energy of related systems.⁴

On the other hand, PMR measurements² on 1,2,5-triphenylphosphole (II) show that the phosphole ring protons resonate in the aromatic region together with the phenyl protons ($\tau = 2.35$ –2.9) but in the PMR spectrum of the phosphole oxide, one of the peaks due to the phosphole ring protons appears outside the aromatic region at $\tau = 3.15$. These observations may possibly mean that the phosphole ring in II has a small degree of aromaticity. More recently, Märkl⁵ has measured the PMR spectrum of 1-phenyl-2,5-dimethylphosphole and has concluded that the results are not inconsistent with some degree of aromatic character in the phosphole ring.

In view of this conflicting evidence, we decided to investigate the dienoid character of the phosphole ring and the availability of the non-bonding electron pair of the phosphorus atom under much milder conditions than those employed by earlier workers. We have therefore investigated the reaction of the readily available 1,2,5-triphenylphosphole (II) with dimethyl acetylenedicarboxylate at room temperature. This ester was chosen because it is powerful dienophile and is also known to react

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rapidly at low temperature with the mildly nucleophilic electron pair of triphenylphosphine.⁶ Furthermore, direct comparison with the reaction of similar pyrrole systems with the ester⁷ could be made.

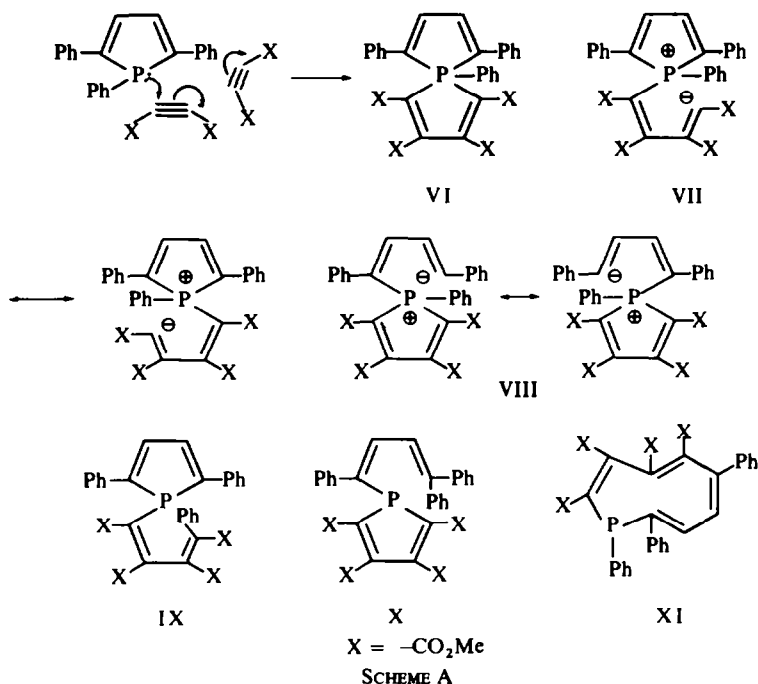
Preliminary experiments showed that 1,2,5-triphenylphosphole-1-oxide (where the phosphorus electron pair is not available to the ring) reacts slowly with dimethyl acetylenedicarboxylate in refluxing benzene over several hours to give dimethyl 3,6-diphenylphthalate (III). However, the phosphole (II) itself does not react under these conditions. This suggests that the phosphole oxide has considerably more dienoid character than the phosphole and that the *d*-electron pair of II is not particularly readily available for reaction compared with the electron pair of triphenylphosphine where reaction with the ester in ether solution occurs very rapidly⁶ at -50° to give IV which rearranges at room temperature to give V.

The phosphole (II) was found to react with a large excess of undiluted dimethyl acetylenedicarboxylate at room temperature under nitrogen during two days to give three products. The first product occurred as colourless crystals in small yield (9%) and proved to be dimethyl 3,6-diphenylphthalate (III). This was obviously formed from a simple Diels-Alder reaction of the ester with II followed by elimination of the phosphorus fragment (as in the case of the phosphole oxide) and this reaction indicates some dienoid character in II.

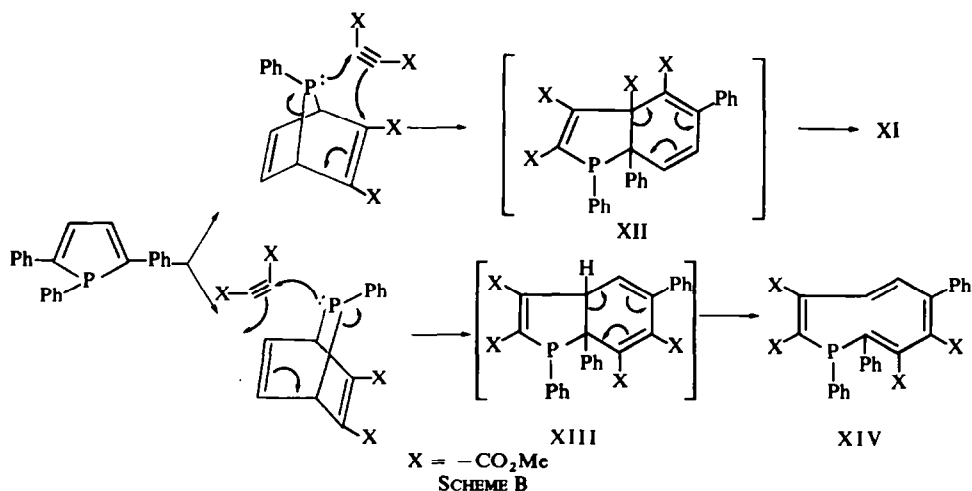
The second product occurred in moderate yield (37%) as yellow crystals, m.p. 182° with extensive decomposition. Analyses and the PMR spectrum showed this to be a 2:1 adduct of the ester with II and this paper is primarily concerned with the structure of this adduct.

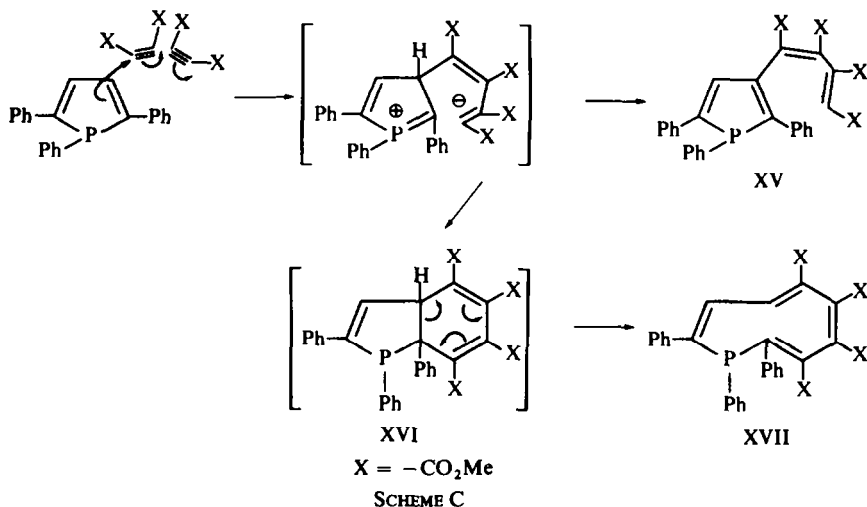
The third product occurred in very low yield (2.5%) as red crystals, m.p. $218-220^\circ$ (dec), which analyses showed to be a 4:1 adduct of the ester with II. Initially, the red adduct crystallized together with the yellow 2:1 adduct from ether but efficient separation was achieved by chromatography on silica gel with methylene chloride. The 2:1 adduct does not appear to be an intermediate in the formation of the 4:1 adduct since mixtures of the pure 2:1 adduct with a large excess of the pure ester showed no trace of the red compound after 10 days at room temperature (TLC examination).

In considering possible structures for the yellow 2:1 adduct, several modes of reaction with the ester are open to II and the principal modes are shown in Schemes A, B and C. Scheme A illustrates the possible products obtainable from the reaction of the lone-pair electrons of the phosphorus atom with the ester. The various possible



products shown parallel those discussed⁶ in the reaction of triphenylphosphine with the ester. Scheme B represents an initial diene reaction of II with the ester followed by reaction of the initial 1:1 adduct with a second molecule of the ester in the same way that N-methylpyrrole reacts with the ester.⁷ Structure III, which is observed as a product, could easily arise as a by-product in the early stages of this reaction. Scheme C represents the electrophilic attack of the ester at the 3-position of the phosphole. Schemes A and B would be reactions of a phosphole ring of little or no aromatic character while Scheme C would be a reaction of an electron-rich aromatic phosphole





ring. Several other less likely modes of reaction are possible but would lead to either the same products as shown in the reaction sequences or would give colourless products containing little unsaturation.

The structures of particular interest are the 1-phospha-2,4,6,8-cyclononatetraenes (XI, XIV and XVII), which are potentially aromatic 10 π -electron systems, and the 1,1'-spirobiphosphole (VI). This spirobiphosphole is of interest for two reasons. First, only two simple phospholes containing pentavalent phosphorus are known^{6, 8} and only one of these⁸ is stable at room temperature. Other pentavalent phosphole derivatives are known but one⁹ or two¹⁰ benzene rings are fused to the phosphole ring. Second, although spirobiphospholes (containing quaternary or pentavalent¹¹ phosphorus) and even spirotriphospholes¹² (in the form of "ate" complexes) are known, they all contain benzene rings fused to the phosphole ring which destroys the dienoid character of this ring.

Many of the possible structures can be eliminated on spectroscopic evidence. The PMR spectrum of the 2:1 adduct shows 17 aromatic and olefinic protons as a complex multiplet at $\tau = 2.1$ –3.0 and 12 OMe protons as four signals of equal area at $\tau = 6.14$, 6.35, 6.56 and 6.59. This immediately eliminates structure X which, owing to its symmetry, would be expected to show only two OMe signals, each of 6 protons. This spectrum probably eliminates structures VII and VIII since in each case, resonance between the two mirror-image zwitterionic contributors would create one average magnetic environment for the ester groups α to the phosphorus atom and another for those β to the phosphorus atom. This would again give rise to two OMe signals, each of 6 protons. It will be seen that structures X, VII and VIII are also eliminated on other grounds.

The UV spectrum of the adduct in benzene shows λ_{\max} (log ϵ) at 337 (3.99) μ while in ethanol it shows λ_{\max} (log ϵ) at 270 (4.18) and 348 (3.93) μ . This eliminates structures VII and XV which, by analogy with the spectra² of various derivatives of II, would be expected to absorb at considerably longer wavelength than II which shows in ethanol² λ_{\max} (log ϵ) at 222 (4.38) and 369 (4.25) μ . Structures VII and VIII are also

dipolar structures which would be expected to absorb at much longer wavelength than is observed. Moreover, it would be expected that in the UV spectra of the dipolar structures VII and VIII, a hypsochromic shift in the longest wavelength band would be observed on changing from benzene to ethanol as solvent. Such hypsochromic shifts have been observed for similar dipolar structures.¹³

The bicyclic structures XII, XIII and XVI are clearly untenable (except possibly as transient intermediates) for two reasons. First, they would absorb UV radiation at much shorter wavelength than is observed for the yellow adduct. Second, in each case there is a bulky phenyl group in an angular position which would almost certainly cause rearrangement as shown to give the much less strained 9-membered ring compounds XI, XIV and XVII. These bicyclic structures are also eliminated on chemical grounds.

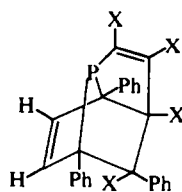
Thus, spectroscopic evidence conclusively eliminates structures VII, VIII, X, XII, XIII, XV and XVI and we are left with structures VI, IX, XI, XIV and XVII.

Chemical evidence narrows the choice still further. The 9-membered ring structures could possibly be aromatic but would probably have little aromatic character. If they were aromatic, the *d*-electron pair of the phosphorus atom would not be readily available for quaternization and oxidation. Likewise, in the spirobiphosphole (VI), the phosphorus is pentavalent and would be unable to quaternize or oxidize without destroying the spiran system. However, IX is a normal phosphole structure and would be expected to form readily a quaternary salt with boiling methyl iodide as does II.² Moreover, 1,2,3,4,5-pentaphenylphosphole and II, both of which are structurally and electronically closely related to IX, form oxides very rapidly and almost quantitatively^{1,2} on treatment with hydrogen peroxide in hot acetone or ethanol. We find that the yellow 2:1 adduct is virtually unaffected by boiling with a very large excess of methyl iodide for 30 hr and is very little affected by boiling with methyl iodide in nitromethane for 10 hr. In the latter case, a small amount of an amorphous, brown, high-melting compound is formed but much of the starting material remains unchanged (TLC examination). Furthermore, the adduct is unaffected by a large excess of hydrogen peroxide in ethanol at room temperature over 24 hr. Even boiling this solution for 2.5 hr leaves substantial amounts of starting material unchanged although TLC examination shows the presence of two other compounds. Similar experiments with hydrogen peroxide in hot acetic acid show that the reaction mixture after 1.5 hr contains up to 5 components but that some starting material remains unchanged.

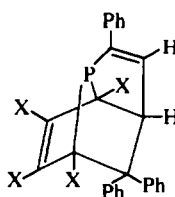
Thus, the behaviour of the yellow 2:1 adduct towards methyl iodide and hydrogen peroxide is far from typical phosphole or tertiary phosphine behaviour and structure IX may therefore be eliminated. This lack of phosphole or phosphine character is further evidence against structures X, XII, XIII, XV and XVI which have already been eliminated on spectroscopic grounds. This evidence also casts doubt upon structures XI, XIV and XVII since such 9-membered rings would probably have tertiary phosphine characteristics. We are therefore left with the spirobiphosphole (VI) as the most probable structure with XI, XIV and XVII as less likely possibilities.

Conclusive proof that the structure is that of the spirobiphosphole comes from the fact that the yellow 2:1 adduct slowly rearranges over several hours in boiling chloroform or ethanol to give a colourless isomer. The UV spectrum of this rearrangement product shows λ_{max} (log ϵ) at 206 (4.63) and 248 (4.31) m μ which shows that much of the conjugation present in the original 2:1 adduct has been lost on rearrange-

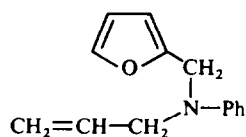
ment. That the rearrangement takes place on warming is alone very suggestive of a pentacovalent phosphole type structure since Johnson⁶ has shown that the phosphole (IV) rearranges rapidly at room temperature to give the open chain isomer (V). Furthermore, it is difficult to visualize any rearrangement in the 9-membered ring structures which could lead to a colourless product absorbing at such a short wavelength as 248 m μ and for steric reasons, collapse to a bicyclic system is most unlikely. However, it is clear that if the structure is that of the spirobiphosphole (VI), the rearrangement is not simply the type observed⁶ for the phosphole (IV) since this would give IX or X, both of which would be coloured. We think that such a rearrangement does occur but that the product undergoes a further internal Diels-Alder reaction to give XVIII or XIX in which conjugation is very much reduced. This is quite likely to occur since it has been shown earlier in this paper that the phosphole system undergoes the Diels-Alder reaction under very mild conditions to give III and the related furan structure XX undergoes such a reaction spontaneously at room temperature¹⁴ to give XXI.



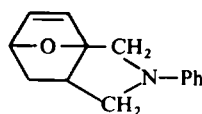
XVIII



XIX



XX



XXI

Once again, chemical and spectroscopic evidence is consistent with such a rearrangement. The colourless rearrangement product is clearly an ordinary tertiary phosphine since it forms an oxide in almost quantitative yield on brief treatment with hydrogen peroxide in ethanol and even on boiling briefly in xylene in the presence of air. The IR spectrum shows a weak peak at 1643 cm⁻¹ which is indicative of an isolated double bond and is therefore consistent with both XVIII and XIX. The band at 248 m μ in the UV spectrum of the rearranged adduct favours XIX since it is suggestive of a styrene type chromophore. Styrene itself shows λ_{\max} (log ϵ) at 244 (4.1) m μ . The PMR spectrum should be the deciding factor since the spectrum of XVIII should show two olefinic protons around $\tau = 4.5$ while that of XIX should show one olefinic proton corresponding to a β proton in a styrene system at $\tau = 4.5-5$ and one methine proton around $\tau = 8-8.5$. The colourless rearrangement product is not very soluble in CDCl₃ and residual CHCl₃ in the solvent therefore makes accurate integration difficult. However, the PMR spectrum shows approximately 15 aromatic protons as a complex multiplet at $\tau = 2.5-3.1$ and 12 OMe protons as four signals at $\tau = 6.16, 6.23, 6.30$ and 7.09 . In addition, there is a very weak doublet of approxi-

mately one proton (difficult to integrate accurately because of noise) centred on $\tau = 5.09$ with $J = 8$ c/s, and a weak singlet of approximately one proton at $\tau = 8.39$. This spectrum therefore very definitely favours structure XIX for the rearranged adduct. It is interesting to note that there is no coupling between the adjacent olefinic and methine protons (presumably because of the dihedral angle) but that the olefinic proton couples with the phosphorus atom ($J_{HP} = 8$ c/s).

It is therefore clear that the structure of the yellow 2:1 adduct is that of the spiro-biphosphole (VI) which is a type of structure previously unknown.

To summarize, the reaction of the phosphole (II) with dimethyl acetylenedicarboxylate under very mild conditions can follow at least two routes. One of these is a Diels-Alder reaction while the other and major reaction is a reaction at the lone-pair electrons of the phosphorus atom. Both of these are essentially reactions of a non-aromatic system and it can be concluded that the phosphole ring in 1,2,5-triphenylphosphole (II) has virtually no aromatic character. In the case of the phosphole (II) the major reaction with the ester is at the phosphorus atom whereas in the case of N-methylpyrrole,⁷ addition to the diene system occurs. Other pyrrole derivatives tend to give Michael addition across the triple bond of the ester.⁷

EXPERIMENTAL

IR measurements were made with a Perkin-Elmer 237 instrument in Nujol and UV spectra were recorded with a Unicam SP 800A spectrophotometer. PMR spectra were recorded in CDCl_3 soln with a Varian A-60 spectrometer. Reactions were followed and purities were checked by TLC on Kieselgel HF₂₅₄ (Merck) using CH_2Cl_2 or CHCl_3 .

Reaction of 1,2,5-triphenylphosphole-1-oxide with dimethyl acetylenedicarboxylate. The phosphole oxide (2 g) and the ester (1.5 g) were dissolved in benzene (150 ml) and heated under reflux for 7.5 hr. The hot soln was filtered, evaporated to dryness, extracted with boiling ether (100 ml) and the resulting mixture was filtered while hot. The residue (1.08 g) was found to be almost pure starting oxide. The filtrate on cooling slowly deposited crystals (0.57 g) of III, m.p. 191° (lit.¹⁵ m.p. 191°).

The phosphole (II) itself does not react with the ester under these conditions.

Reaction of 1,2,5-triphenylphosphole with dimethyl acetylenedicarboxylate. The finely powdered phosphole (5 g) and the ester (50 ml) were mixed and stored under N_2 with occasional shaking for 2 days. The mixture was then filtered and the residue was washed with a little ice-cold ether. The colourless crystalline residue (0.5 g, 9%) proved to be dimethyl 3,6-diphenylphthalate, m.p. 191° . (Found: C, 76.0; H, 5.0. Calc. for $\text{C}_{22}\text{H}_{18}\text{O}_4$: C, 76.4; H, 5.2%).

The filtrate was poured into ether (600 ml) with stirring and the mixture was immediately filtered to remove a small quantity of suspended dark brown material. The clear, dark red, ethereal soln was allowed to stand without evaporation for 2 days and large orange crystals were slowly deposited. These were removed by filtration and the mother liquor was concentrated to obtain a second crop. The product was recrystallized from hot EtOH to give yellow crystals (3.52 g, 37%,) of tetramethyl 1,2,5-triphenyl-1,1'-spirobiphosphole-2',3',4',5'-tetracarboxylate (VI), m.p. $179-181^\circ$ (dec). (Found: C, 68.6; H, 5.4; P, 5.2. $\text{C}_{34}\text{H}_{26}\text{O}_8\text{P}_2$ requires: C, 68.5; H, 4.9; P, 5.2%); IR shows ν_{max} at 1740, 1675, 1660, 1640, 1600, 1500, 1346, 1316, 1281, 1240, 1220, 1200, 1143, 1115, 1071, 755, 728, 703, 693 cm^{-1} .

The collected mother liquors of the above recrystallization were evaporated to dryness and the residue was taken up in CHCl_3 . The CHCl_3 soln was chromatographed on silica gel (0.05-0.2 mm) and with CHCl_3 as eluant, a little more of VI was obtained. The column was then eluted with acetone and a deep red solution was obtained. Evaporation of this gave dark red crystals (0.355 g, 2.5%) of an adduct, m.p. $218-220^\circ$ (dec), containing four molecules of the ester to one of the phosphole. (Found: C, 62.8; H, 5.1; P, 3.8. $\text{C}_{46}\text{H}_{41}\text{O}_{16}\text{P}_2$ requires: C, 62.7; H, 4.7; P, 3.5%); IR shows ν_{max} at 1740, 1729, 1715, 1641, 1596, 1342, 1300, 1274, 1259, 1199, 1128, 1095, 1051, 868, 800, 750, 723, 699 cm^{-1} ; UV in benzene shows λ_{max} (log ϵ) at ca. 310 (3.9) m μ as a shoulder with a very long tail-off and 450 (2.7) m μ .

Rearrangement of tetramethyl 1,2,5-triphenyl-1,1'-spirobiphosphole-2',3',4',5'-tetracarboxylate (VI). The spirobiphosphole (0.3 g) in CHCl_3 (150 ml) was heated under reflux for 4 hr. The cooled soln was concentrated to about 20 ml and chromatographed on silica gel (0.05–0.2 mm) using CHCl_3 as eluant. The colourless first fraction on evaporation yielded crystals (0.07 g, 23%) of the colourless *rearrangement product* (XIX), m.p. 220° (dec). (Found: C, 68.6; H, 5.0; P, 5.5. $\text{C}_{34}\text{H}_{29}\text{O}_8\text{P}$ requires: C, 68.5; H, 4.9; P, 5.2%). The second fraction gave unchanged starting material in almost quantitative yield.

The yield of rearrangement product was improved on longer boiling but the product was contaminated with traces of two other minor products which made purification difficult. After 6 hr boiling of the soln, TLC indicated about 50% yield of the rearrangement product.

IR of the rearrangement product XIX shows ν_{max} at 1740, 1730, 1642, 1599, 1493, 1462, 1328, 1258, 1242, 1203, 1174, 1079, 868, 756, 699 cm^{-1} .

Oxidation of the rearrangement product XIX. The colourless compound (0.4 g) in EtOH (50 ml) and CHCl_3 (5 ml) was treated with H_2O_2 (4 ml, 30%). The mixture was allowed to stand for 30 min with occasional shaking and then water (100 ml) was added. The mixture was extracted with CHCl_3 (2 × 25 ml) and the CHCl_3 layer was washed with water and dried over Na_2SO_4 . The dried soln was evaporated to dryness and the crude solid was recrystallized from hot EtOH. Colourless crystals (0.397 g, 96%) of the *oxide* of XIX were obtained, m.p. 256–259° (dec). (Found: C, 65.5; H, 4.9; P, 6.2. $\text{C}_{34}\text{H}_{29}\text{O}_9\text{P}$ requires: C, 66.6; H, 4.9; P, 5.1%). This analysis is not particularly good because of the presence of traces of another compound which could not be removed by chromatography. However, there is no doubt that the compound is an oxide because the IR spectrum is virtually identical to that of the starting material except that the peaks due to the ester groups around 1260–1225 cm^{-1} are broadened and rounded by the superimposed peak due to the $\text{P}=\text{O}$ stretching vibration.

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