The Synthesis of Diethyl *p*-Tolylsulphonylethynylphosphonate and Related Acetylenes, and their Reactions with Nucleophiles, Pyridinium-1-dicyanomethylides, and Dienes

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Diethyl *p*-tolylthioethynylphosphonate (**10**) was synthesized from diethyl ethynylphosphonate (**7**) by two routes and oxidised to the corresponding sulphoxide (**11**) and sulphone (**12**). The sulphone showed no triple bond i.r. absorption, but a strong Raman band, and nucleophiles could add to either end of the triple bond. These alkynes gave indolizines with pyridinium-1-dicyanomethylides and Diels–Alder adducts with anthracenes. The orientations of the additions were deduced from ^1H, ^1H; ^{31}P, ^1H; and ^{31}P, ^{13}C coupling constants.

Dimethyl acetylenedicarboxylate (**1**) behaves as a highly reactive dieneophile and Michael-type reaction acceptor on many occasions, and its numerous reactions with heterocycles,[1,2] and in the synthesis of heterocycles[3] has been reviewed. Very few other disubstituted acetylenes have been investigated in this way and the enormous scope for new research has been pointed out.[2] Acetylenic sulphides [*e.g.* (**2**)] are much more stable to hydrolysis than their oxygen analogues,[4] and the sulphone (**4**) adds thiolate anions[5] yielding only *Z*-alkenes; with amines[6] the situation is more complicated and both *E*- and *Z*-isomers can be formed, and sodium benzenesulphinate with 1-phenylsulphonylprop-1-yne gave the *Z*-addition product only.[7]

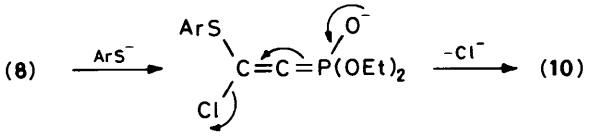
$RC{\equiv}CR^1$

	R	R^1		R	R^1
(**1**)	CO_2Me	CO_2Me	(**7**)	H	$PO(OEt)_2$
(**2**)	EtS	H	(**8**)	Cl	$PO(OEt)_2$
(**3**)	ArS	H	(**9**)	$PO(OEt)_2$	$PO(OEt)_2$
(**4**)	$ArSO_2$	H	(**10**)	ArS	$PO(OEt)_2$
(**5**)	PhS	CO_2Et	(**11**)	ArSO	$PO(OEt)_2$
(**6**)	$PhSO_2$	CO_2Et	(**12**)	$ArSO_2$	$PO(OEt)_2$

Ar = C_6H_4Me-*p* in all formulae

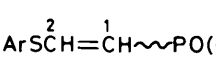
Ethyl 2-phenylthioethyne-1-carboxylate (**5**), an example of a 'push-pull' acetylene[8] has been synthesized and oxidised to the sulphone[9] (**6**). This sulphone is very reactive, polymerising and undergoing Diels–Alder additions at room temperature, and is almost the first example of an acetylene possessing two different powerful electron-attracting groups. Some properties of the ethyl ethynylphosphonates (**7**) and (**9**)[10] and related esters,[11] and of diethyl ethoxycarbonylethynylphosphonate[12] have been reported and now the preparation and some reactions of the sulphur-containing phosphonates (**10**)—(**12**) are described.

Compounds of type (**10**)—(**12**) can be synthesized from acetylene by introducing the phosphorus-containing group first, or second, and our best synthesis started with diethyl ethynylphosphonate (**7**).[10] This was converted into the chloroalkyne (**8**) by t-butyl hypochlorite and subsequent treatment with 4-methylthiophenol in the presence of potassium hydroxide caused presumably an addition–elimination sequence (Scheme 1) yielding diethyl *p*-tolylthioethynylphosphonate (**10**). An alternative route to (**10**) involved the Michael-type addition of the same thiol to diethyl ethynylphosphonate, which gave only the *Z*-alkene (**13**). This, or the *E*-isomer (**14**) formed on attempted distillation,[10] with bromine in carbon tetrachloride

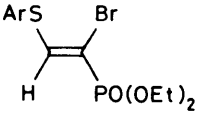


Scheme 1.

yielded the bromoalkene (**15**). This compound lost hydrogen bromide to ethanolic potassium hydroxide, in a fickle and unsatisfactory reaction, giving the acetylene (**10**). The dehydrobromination was very sensitive to the amount of potassium hydroxide employed; 18-crown-6 with powdered potassium hydroxide under ether caused a partial attack on phosphorus leading to a mixture of the desired acetylene (**10**) and the sulphide (**3**), or partial dehydrobromination if shorter times were employed, and 1,8-diazabicyclo[5.4.0]undec-1-ene in acetonitrile[13] gave little (**10**). The stereochemistry of compounds (**13**) and (**14**) followed from their ^1H n.m.r. spectra[10] in which the 2-H resonances were totally clear; compound (**13**) showed a much higher coupling with phosphorus, and lower with hydrogen than the isomer (**14**), and the alkene (**15**) which could not be obtained pure was identified from its low P,H coupling. *p*-Tolylthioacetylene (**3**) on successive treatment with butyl-lithium and diethyl chlorophosphate did give the disubstituted acetylene (**10**), but on only two occasions out of eight, and the reason for the failure could not be ascertained. The Grignard derivative of the ethynyl sulphide (**3**), in contrast to ethynylmagnesium bromide,[14] did not give an ethynylphosphinate with methyl methylchlorophosphonate.



(**13**) *Z*-
(**14**) *E*-



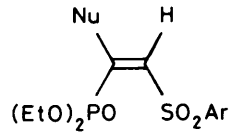
(**15**)

The ester (**10**), which must be pure for successful results, with 1 and 2 mol equiv. of 3-chloroperbenzoic acid gave the sulphoxide (**11**) and the sulphone (**12**) respectively. Attempts to prepare the last compound from the sulphone (**4**) by successive treatment with butyl-lithium and diethyl chlorophosphate, or from diethyl 2-chloroethynylphosphonate (**8**) and sodium 4-methylbenzenesulphinate, gave complex mixtures, as did treatment of the chloroacetylene (**8**) with sodium cyanide.

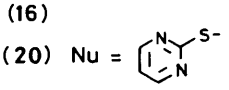
The sulphide (**10**) showed an intense acetylenic absorption at 2 120 cm^{-1} in the i.r. spectrum. The sulphoxide (**11**) was never obtained analytically pure and showed as sole peak in the triple bond region a weak absorption at the same wavelength which can be associated with unoxidised sulphide (**10**), while the sulphone (**12**) showed no absorption in the triple bond region. The i.r. spectrum for the sulphide (**5**) has not been reported, the data[9] for the sulphone (**6**) does not include a triple bond frequency, so a similar situation may pertain here.

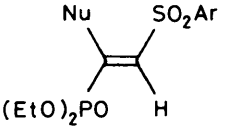
The Raman spectrum of the sulphoxide (**11**) could not be obtained because of the fluorescence caused by the red and green lasers employed, but the acetylenes (**1**), (**9**), and (**12**) showed strong absorptions at 2 249, 2 159, and 2 165 cm^{-1} respectively. The apparent symmetry of the triple bond in the sulphone (**12**) in the i.r. region is remarkable and a similar situation relates to diethyl ethoxycarbonylethynylphosphonate which shows a Raman absorption at 2 213 cm^{-1} but no absorption in this region in the i.r.[12]

In view of this 'symmetry,' and that both the sulphone (**4**) and the phosphonate (**7**) add nucleophiles at the 2-carbon atoms, it was not possible to predict with confidence the orientation of addition to the sulphone-phosphonate (**12**); attack at the phosphonate group could also occur.[10] Four possible addition products, exemplified by structures (**16**)—(**19**) are possible. Only for type (**16**) the *trans* $J_{P,H}$ will be large and in the 25—50 Hz range,[15] enabling a clear identification to be made. Types (**18**) and (**19**) can be differentiated from type (**17**) through their ^{13}C n.m.r. spectra. The carbon directly attached to phosphorus in (**17**) will couple both to the directly attached phosphorus $J_{P,C}$ *ca.* 200 Hz, and to the directly attached hydrogen which can be ascertained by off-resonance decoupling. This method was employed to identify our adducts, but we were not able to resolve the ambiguity between structure types (**18**) and (**19**).



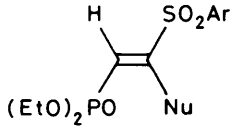
(**16**)



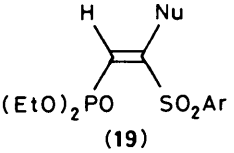


(**17**)

(**21**) Nu = Et_2N



(**18**)



(**19**)

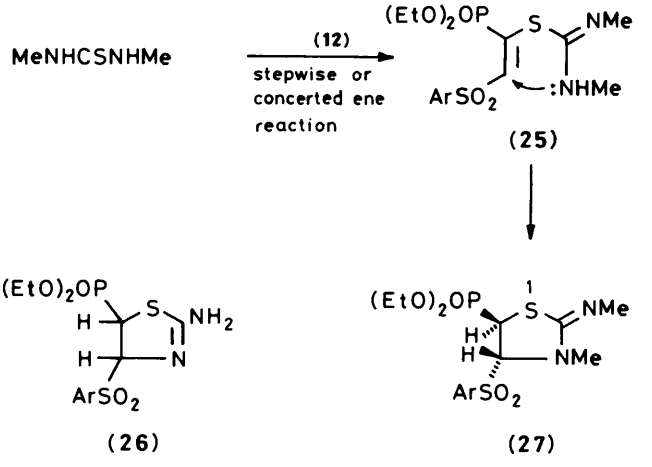
(**22**) Nu = *E*- or *Z*-Cl

(**23**) Nu = *E*- or *Z*-OMe

(**24**) Nu = *E*- or *Z*-OEt

As Lewis acids accelerate many reactions of dimethyl acetylenedicarboxylate,[16,17] the effect of aluminium chloride on the stability of diethyl *p*-tolylsulphonylethynylphosphonate in dichloromethane was examined. Hydrogen chloride, probably arising from traces of moisture in the aluminium chloride, added across the triple bond. A subsequent experiment with deuterium oxide work-up gave no deuteriated product so a possible intermediate involving a cation–aluminium bond could not be detected. The product was the ester (**22**), identified in part from its ^1H and ^{13}C n.m.r. spectra. The olefinic proton was weakly coupled to phosphorus ($J_{P,H}$ 8 Hz), and to the carbon bearing the phosphorus atom ($J_{P,C}$ 183 Hz).

Addition of methanol to diethyl *p*-tolylsulphonylethynylphosphonate (**12**) catalysed by a trace of dissolved sodium hydride, in the same direction gave (**23**) as shown similarly from its ^1H and ^{13}C n.m.r. spectra. The phosphonate group therefore controlled the direction of this nucleophilic addition. Diethylamine with the ester (**12**) in chloroform after a few seconds gave an equimolar adduct as an unstable oil, showing a 1-H doublet ($J_{P,H}$ 16 Hz). The magnitude of this coupling suggested that the compound had the *E*-geometry of structure (**21**). This conclusion was supported by the ^{13}C n.m.r. spectrum, albeit on a partially decomposed specimen, which showed a doublet ($J_{P,C}$ 25 Hz) as the only signal between 77 and 125 p.p.m. and this changed to a double doublet in the off-resonance proton decoupled spectrum. Here the sulphone group controls the direction of nucleophilic attack. The ester (**12**) with benzimidazole and its 2-methyl derivative in ethanol gave oily equimolar adducts which could not be purified.[18,19] Reactions with pyridine, 3,5-dimethylpyridine, or 2-methylquinoline in acetonitrile, or with imidazole, pyrrole, 1-methylpyrrole or indole, in contrast to dimethyl acetylenedicarboxylate,[1] gave unresolvable complex mixtures. Behaving as bases, 3,5-dimethylpyridine and 1-methylimidazole, in methanol and ethanol respectively, catalysed addition of the solvents to the ester (**12**) giving the vinyl ethers (**23**) and (**24**) respectively, identified from their mass and ^1H n.m.r. spectra.

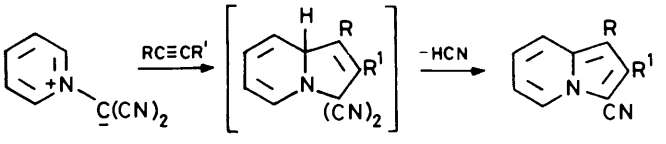


Scheme 2.

Many thioureas give addition and condensation products with acetylenecarboxylic esters,[20] and the diethyl *p*-tolylsulphonylphosphonate (**12**) gave crystalline equimolar adducts with thiourea and its *N*,*N*′-dimethyl derivative. The second adduct was identified as the thiazolidine (**27**) from its ^{13}C n.m.r. spectrum. The 4- and 5-carbon atoms were both in the sp^3-C region and attached to hydrogen atoms, and the 5-carbon atom coupled strongly ($J_{P,C}$ 161 Hz) to the phosphorus atom. The 4- and 5-protons both coupled to phosphorus but not to each other. Electron-attracting substituents do reduce inter-proton couplings in some 1,2-disubstituted ethanes,[21] but if the protons were *trans*, as shown, the Karplus equation[21] would in any case predict little coupling and the large phosphorus- and sulphur-containing groups would be placed where they will have minimum steric interaction. The ^1H n.m.r. spectrum of the crude reaction mixture showed a small doublet at δ 9.63 ($J_{P,H}$ 33 Hz). The coupling is consistent only with a *trans* olefinic phosphorus–hydrogen coupling, and this suggests that the adduct (**27**) is formed *via* the Michael-type adduct (**25**) shown in Scheme 2.

Thiourea also gave a similar dihydrothiazole (**26**), with spectra similar to (**27**), but the stereochemistry could not be ascertained. Pyridine-2-thiol, pyrimidine-2-thiol, and benzimidazole-2-thiol gave oils which were identified from their spectra as mixtures of compounds of types (**16**)—(**17**). Only one of these adducts (**20**) was obtained spectroscopically pure.

Diethyl *p*-tolylthioethynylphosphonate (**10**), a 'push-pull' acetylene,[8] where the electron demand of the phosphonate group is partially satisfied by the electron-donating sulphur atom, did not react with pyrrolidine but it did yield the indolizine (**30**) on heating with pyridinium-1-dicyanomethylide (**28**)[22] in toluene (Scheme 3). The addition must follow the



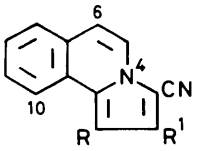
(**28**)
(**29**) benzo[*c*]-

	R	R¹
(**30**)	$PO(OEt)_2$	ArS
(**31**)	$PO(OEt)_2$	ArSO
(**32**)	$PO(OEt)_2$	$ArSO_2$
(**33**)	$ArSO_2$	$PO(OEt)_2$
(**34**)	$ArSO_2$	H
(**35**)	$PO(OEt)_2$	Cl

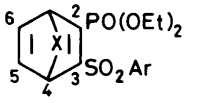
Scheme 3.

path shown for electronic reasons as is the case for methyl propiolate.[1] The ethynyl sulphoxide (**11**) gave a similar indolizine (**31**), and oxidation of both these indolizines by 3-chloroperbenzoic acid yielded the same sulphone (**32**) thereby showing that the phosphonate group controlled the mode of addition in both cases. Treatment of the ylide (**28**) with the sulphonylethynylphosphonate (**12**) however gave the isomeric sulphone (**33**) so that the direction of reactivity of the triple bond to nucleophiles has been reversed. The ^{13}C n.m.r. spectra, those of the indolizinylphosphonates described earlier,[1] and the indolizines (**34**) and (**35**) prepared from (**28**) and the appropriate acetylenes, showed the expected close similarities. The isoquinolinium ylide (**29**) with acetylenes (**7**), (**4**), and (**9**) gave the pyrrolo[2,1-*a*]isoquinolines (**36**)—(**38**). The 1-phosphonate (**36**) was converted into the 1-phosphonic acid (**39**) by iodotrimethylsilane followed by methanol, and this on refluxing with aqueous methanolic hydrochloric acid yielded 3-cyanopyrrolo[2,1-*a*]isoquinoline (**40**). Protonation at position 1, well known for indolizines,[23] is presumably followed by dephosphorylation. The ylide (**29**) with diethyl *p*-tolylsulphonylethynylphosphonate (**12**) gave the pyrroloisoquinoline (**41**) or (**42**) according to analytical and mass spectral data. The melting point was not sharp, and the ^1H n.m.r. spectrum showed two sets of ArMe and OCH_2Me signals in roughly 2:1 ratio which did not alter over the 40—120 °C range. This suggested that both pyrroloisoquinolines had been formed, but attempts at separation were fruitless. Removal of the diethyl phosphonate group, as for (**36**), gave a compound similar to the pyrroloisoquinoline (**37**) but with a higher melting point and such a low solubility in common solvents that its n.m.r. spectra could not be measured; it appears to be (**43**) and derived from (**41**).

Diethyl ethynylphosphonate (**7**) and the diphosphonate (**9**) undergo Diels–Alder additions, and their adducts with anthracene and 9-methylanthracene were prepared for comparison with those obtained from the sulphur-containing acetylenes (**10**)—(**12**). The phosphorus-proton couplings, observed in the ^1H n.m.r. spectra, for the 9- and 10-protons, were 9—11 Hz for the 3-bond and 4—6 Hz for the 4-bond couplings, and were identified initially from the spectrum of the adduct

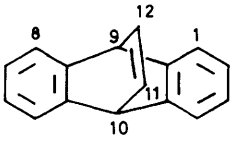


	R	R¹
(**36**)	$PO(OEt)_2$	H
(**37**)	$ArSO_2$	H
(**38**)	$PO(OEt)_2$	$PO(OEt)_2$
(**39**)	$PO(OH)_2$	H
(**40**)	H	H
(**41**)	$PO(OEt)_2$	$ArSO_2$
(**42**)	$ArSO_2$	$PO(OEt)_2$
(**43**)	H	$ArSO_2$



(**44**) X = $(CH_2)_2$
(**45**) X = O

(**46**). With 9-methylanthracene diethyl ethynylphosphonate (**7**) gave the adduct (**47**) with a trace of the isomer (**48**) detected spectroscopically. The sulphone (**12**) reacted at room temperature yielding (**52**) exclusively, while the sulphoxide (**11**) needed refluxing in boiling toluene to form (**53**), oxidised by perbenzoic acid to the same sulphone (**52**). The sulphide (**10**) was less reactive, but at 160 °C with 9-methylanthracene gave a single product (**54**), identified in part because perbenzoic acid oxidation yielded a sulphone (**55**) isomeric with (**52**) obtained from the sulphonylethynylphosphonate (**12**). In contrast to the reactions with the pyridinium ylides, the effect of the sulphoxide group on the orientation of addition resembles that of the sulphone and not that of the sulphide. Diethyl *p*-tolylsulphonylethynylphosphonate (**12**) gave the expected addition product (**44**) with cyclohexa-1,3-diene, an unstable adduct spectroscopically characterised as (**45**) with furan, and the product with 1-acetoxybuta-1,3-diene was diethyl 2-(*p*-tolylsulphonyl)-benzenephosphonate formed by a similar addition and loss of acetic acid.



	9	11	12
(**46**)	H	$PO(OEt)_2$	H
(**47**)	Me	$PO(OEt)_2$	H
(**48**)	Me	H	$PO(OEt)_2$
(**49**)	H	$PO(OEt)_2$	$PO(OEt)_2$
(**50**)	Me	$PO(OEt)_2$	$PO(OEt)_2$
(**51**)	H	$PO(OEt)_2$	SO_2Ar
(**52**)	Me	SO_2Ar	$PO(OEt)_2$
(**53**)	Me	SOAr	$PO(OEt)_2$
(**54**)	Me	$PO(OEt)_2$	SAr
(**55**)	Me	$PO(OEt)_2$	SO_2Ar

It may be concluded that the stereoelectronic effects of the *p*-tolyl-sulphonyl, or -sulphoxyl, and diethyl phosphonate groups, on addition reactions when attached to a triple bond, must be finely balanced. The i.r. and Raman data show a 'symmetrical' triple bond in the sulphone (**12**), and suggest a similar situation for the sulphoxide (**11**).

Experimental

Solvents were removed using a Büchi evaporator at as low a temperature as practicable. ^1H and ^{13}C N.m.r. spectra were measured at 60 and 22.63 MHz in $CDCl_3$ using internal tetramethylsilane as standard. For the ^{13}C spectra in all cases

off-resonance decoupling confirmed the structure assignments given. *J* Values are given in Hz. I.r. spectra were recorded for liquid films or Nujol mulls using a Perkin-Elmer 257 spectrometer. T.l.c. was performed using Camlab 'Polygram' Sil G/u.v.$_{254}$ silica gel pre-coated sheets, and column chromatography using 400—230 mesh silica gel No. 60 (E. Merck No. 9385) according to the procedure of Still *et al.*[24]

Diethyl p-*Tolylthioethynylphosphonate* (**10**).—(i) Diethyl chloroethynylphosphonate[10] (**8**) (10 g) in ethanol (10 ml) was added quickly to *p*-methylthiophenol (6.32 g) and potassium hydroxide (3.32 g) in ethanol (90 ml) at 0 °C with rapid stirring. After 3 min the solution was allowed to attain room temperature. After filtration most of the solvent was evaporated off, water (50 ml) was added, and the product extracted with chloroform (3 × 50 ml). Chromatography and elution with ether gave the *ester* (**10**) as a pale yellow oil (7.85 g) identical in spectra to the analysed specimen.

(ii) Diethyl (*Z*)-2-*p*-tolylthiovinylphosphonate (**13**) (8.0 g, not distilled[10]) in carbon tetrachloride (20 ml) was treated with bromine (4.0 g) in carbon tetrachloride (40 ml) over 3 min. After being stirred for 30 min the mixture was washed with water and evaporated to give an orange oil (10 g), mostly the bromoethenylphosphonate (**15**); δ_H 1.32 (*ca.* 5 H, t, *J* 7, CH_2Me), 2.30 (3 H, s, C_6H_4Me), 4.11 (*ca.* 3.5 H, 5 lines, *J* 7, CH_2Me), 7.05—7.41 (4 H, m, C_6H_4), and 8.00 (1 H, d, *J* 12, 2-H); *m/z* 365 (M^+, 12), 364 (12), 285 (M^+ − Br, 100), 257 (20), and 229 (60).

This compound (1.0 g) in ethanol (20 ml) was treated with potassium hydroxide (0.3 g) when a precipitate formed immediately. The mixture was stirred for 30 min after which water (50 ml) was added and most of the ethanol evaporated off; extraction of the residue with ether and distillation yielded the *title compound* (**10**) as a colourless oil (0.3 g), b.p. 130—135 °C at 0.1 Torr (Found: C, 54.8; H, 6.0; S, 11.4. $C_{13}H_{17}O_3PS$ requires C, 54.9; H, 6.0; S, 11.3%); $\nu_{max.}$ 2 120, 1 260, 1 050, and 1 030 cm^{-1}; δ_H 1.34 (6 H, t, *J* 7, CH_2Me), 2.30 (3 H, s, C_6H_4Me), 4.12 (4 H, 5 lines, *J* 7, CH_2Me), 7.08 (2 H, d, *J* 8, ArH_2), and 7.31 (2 H, d, *J* 8, ArH_2; δ_C 15.98 (d, $J_{P,C}$ 7, CH_2Me), 20.93 (s, ArMe), 63.17 (d, $J_{P,C}$ 5, OCH_2), 87.42 (d, $J_{P,C}$ 250, C-1), 91.16 (d, $J_{P,C}$ 51, C-2), 128.06 (s), 130.34 (s), and 138.22 (s); *m/z* 284 (M^+, 30), 177 (20), 175 (25), 148 (100), and 147 (50).

(iii) *p*-Tolylthioethyne[25] (**3**) (2.0 g) stirred in dry tetrahydrofuran (20 ml) under nitrogen and at −78 °C was treated with butyl-lithium (1.6M in hexane; 9 ml) and after 10 min redistilled diethyl chlorophosphate (2.5 g) in tetrahydrofuran (15 ml) was added quickly. The mixture went black and after 2.5 h at −78 °C was warmed to room temperature. After 1 h water and ether were added, and distillation of the ether-soluble material gave the ester (**10**) (1.45 g), identical with the analysed sample.

Diethyl p-*Tolylsulphinylethynylphosphonate* (**11**).—Diethyl *p*-tolylthioethynylphosphonate (**10**) (5 g) was stirred in chloroform (20 ml) at 0 °C and 3-chloroperbenzoic acid (3.34 g) was added to it; the mixture was then stirred overnight. The resultant milky white mixture was washed with saturated aqueous sodium sulphite (2 × 100 ml) and aqueous hydrochloric acid (5%; 80 ml), dried, and evaporated. Chromatography of the residue with ether as eluant gave the sulphoxide (**11**) as a yellow oil (2.8 g) which was not obtained analytically pure; $\nu_{max.}$ 2 120, 1 270, 1 095, 1 045, 1 020, and 980 cm^{-1}; δ_H 1.31 (6 H, t, *J* 7, 2 × CH_2Me), 2.40 (3 H, s, 4-Me), 4.13 (4 H, 5 lines, *J* 7, 2 × OCH_2), 7.34 (2 H, d, *J* 9, ArH_2), and 7.71 (2 H, d, *J* 9, ArH_2); δ_C 15.87 (d, $J_{P,C}$ 6, CH_2Me), 21.42 (s, 4-Me), 64.02 (d, $J_{P,C}$, 5, OCH_2), 90.57 (d, $J_{P,C}$ 272, C-1), 95.06 (d, $J_{P,C}$ 37, C-2), 125.22 (s), 130.43 (s), 138.58 (s), and 143.48 (s); *m/z* (e.i.) 300 (M^+, 1), 246 (60), 148 (55), 147 (30), 139 (40), 123 (100), 119 (60), 116 (40), and 91 (70).

Diethyl p-*Tolylsulphonylethynylphosphonate* (**12**).—3-Chloroperbenzoic acid (18.22 g) was added to the sulphide (**10**) (12.47 g) in chloroform (150 ml) at 0 °C and the mixture stirred overnight. It was worked up as for (**11**) to give a *colourless oil* (**12**), b.p. 150—160 °C at 0.1 Torr (8.1 g, chars badly) (Found: C, 49.4; H, 5.5. $C_{13}H_{17}O_5PS$ requires C, 49.4; H, 5.4%); $\nu_{max.}$ 1 595, 1 350, 1 240, 1 160, and 1 030 cm^{-1}; Raman 2 159 cm^{-1}; δ_H 1.32 (6 H, t, *J* 7, 2 × CH_2Me), 2.43 (3 H, s, 4-Me), 4.13 (4 H, 5 lines, *J* 7, 2 × OCH_2), 7.34 (2 H, d, *J* 8, ArH_2), and 7.82 (2 H, d, *J* 8, ArH_2); δ_C 16.25 (d, $J_{P,C}$ 7, CH_2Me), 22.06 (s, 4-Me), 64.53 (d, $J_{P,C}$ 6, OCH_2), 80.91 (d, $J_{P,C}$ 266, C-1), 91.19 (d, $J_{P,C}$ 39, C-2), 127.72 (s), 129.93 (s), 136.31 (s), and 146.34 (s); *m/z* (e.i.) 316 (M^+, 44), 288 (16), 260 (74), 196 (11), and 91 (100); *m/z* (d.c.i., NH_3) 334 (M^+ + 18, 100), and 317 (M^+ + 1, 48).

Diethyl 2-*Chloro*-2-p-*tolylsulphonylvinylphosphonate* (**22**).—The sulphone (**12**) (0.5 g), dichloromethane (10 ml), and anhydrous aluminium chloride (0.22 g) were stirred for 3 h. The mixture was then washed with water and dried, and evaporated. Chromatography of the residue with ether as eluant gave the *title compound* (**22**) as a colourless oil (0.22 g) (Found: C, 44.1; H, 5.2. $C_{13}H_{18}ClO_5PS$ requires C, 44.3; H, 5.1%); $\nu_{max.}$ 1 595, 1 395, 1 335, 1 265, 1 160, 1 090, 1 050, 1 020, and 980 cm^{-1}; δ_H 1.30 (6 H, t, *J* 7, 2 × CH_2Me), 2.41 (3 H, s, 4-Me), 4.12 (4 H, 5 lines, *J* 7, 2 × OCH_2), 7.26 (1 H, d, *J* 8, 1-CH), 7.35 (2 H, d, *J* 9, ArH_2), and 7.81 (2 H, d, *J* 9, ArH_2); δ_C 16.19 (d, $J_{P,C}$ 7, CH_2Me), 21.65 (s, 4-Me), 63.04 (d, $J_{P,C}$ 6, OCH_2), 123.98 (d, $J_{P,C}$ 183, C-1), 129.43 (s), 130.62 (s), 132.29 (s), 146.25 (s), and 147.39 (s), *m/z* (i.b.e.i.) 354 + 352 (M^+, 18 + 48), 199 + 197 (29 + 64), 171 + 169 (26 + 82), 155 (22), 143 (29), 141 (86), 139 (88), 109 (65), and 91 (100). An identical experiment using deuterium oxide for the work-up gave a product with an identical ^{1}H n.m.r. spectrum to the above.

Diethyl 2-*Methoxy*-2-p-*tolylsulphonylvinylphosphonate* (**23**).—Sodium hydride (60% in oil; 10 mg) was added to the sulphone (**12**) (0.61 g) dissolved in methanol (10 ml). After 45 min at room temperature the mixture was evaporated and the residue chromatographed with ether, as eluant to give the *title compound* (**23**) as a colourless oil (0.33 g) (Found: C, 47.8; H, 6.1. $C_{14}H_{22}O_6PS$ requires C, 48.3; H, 6.0%); $\nu_{max.}$ 1 625 and 1 595 cm^{-1}; δ_H 1.32 (6 H, *t*, *J* 7, 2 × CH_2Me), 2.43 (3 H, s, 4-Me), 4.05 (3 H, s, OMe), 4.10 (4 H, 5 lines, *J* 7, 2 × OCH_2), 6.26 (1 H, d, *J* 5, 1-H), 7.35 (2 H, d, *J* 8, ArH_2), and 7.80 (2 H, d, *J* 8, ArH_2); δ_C 16.10 (d, $J_{P,C}$ 7, CH_2Me), 21.54 (s, 4-Me), 62.41 (d, $J_{P,C}$ 7, OCH_2), 63.66 (s, OMe), 100.95 (d, $J_{P,C}$ 183, C-1), 128.78 (s), 129.79 (s), 133.94 (s), 145.41 (s), and 165.87 (s, C-2); *m/z* (d.c.i., NH_3) 349 (M^+ + 1, 100), 196 (29), 195 (47), 179 (46), and 139 (26).

Diethyl p-*Tolylsulphonylethynylphosphonate* (**12**) *with Diethylamine*.—The ester (**12**) (0.7 g) and diethylamine (0.16 g) were stirred in ether (5 ml) for 1 h after which the solvent was evaporated off and the residue chromatographed with ether as eluant to give the adduct (**21**) as an unstable oil (0.33 g), δ_H 1.08 + 1.30 (12 H, both t, *J* 7, 4 × Me), 2.39 (3 H, s, 4-Me), 3.54 (4 H, q, *J* 7, 2 × NCH_2), 4.10 (4 H, 5 lines, *J* 7, 2 × OCH_2), 5.93 (1 H, d, *J* 16, 2-H), 7.26 (2 H, d, *J* 8, ArH_2), and 7.79 (2 H, d, *J* 8, ArH_2); δ_C 108.00 ($J_{P,C}$ 25); *m/z* (d.c.i., NH_3) 390 (M^+ + 1, 83), 317 (13), 270 (10), 236 (100), 234 (32), 198 (27), 181 (42), 174 (38), 156 (43), and 139 (83).

Diethyl (E)-3-*Methyl*-2-*methylimino*-4-p-*tolylsulphonyl*-*thiazolidinyl*-5-*phosphonate* (**27**).—The acetylene (**12**) (1.47 g), *N,N'*-dimethylthiourea (0.24 g), and ethanol (5 ml) were stirred overnight at room temperature. Solvent evaporation, followed by chromatography of the residue, eluting with methanol–ether (1:9, v/v), and trituration with ether gave the *thiazolidine* (**27**) as

a colourless powder (0.198 g), m.p. 117—119 °C (Found: C, 45.7; H, 5.6; N, 6.5. $C_{16}H_{25}N_2O_5PS$ requires C, 45.7; H, 5.9; N, 6.7%); $\nu_{max.}$ 1 655 and 1 590 cm^{-1}; δ_H 1.30 (6 H, t, *J* 7, 2 × CH_2Me), 2.42 (3 H, s, 4-Me), 2.71 (3 H, d, $J_{P,H}$ 1, 3-Me), 2.95 (3 H, d, $J_{P,H}$ 1, NMe), 4.12 (4 H, 5 lines, 2 × OCH_2), 4.32 (1 H, d, $J_{P,H}$ 7, 4-H), 4.91 (1 H, d, $J_{P,H}$ 14, 5-H), 7.34 (2 H, d, *J* 8, ArH_2), and 7.82 (2 H, d, *J* 8, ArH_2); δ_C 16.35 ('s', $J_{P,C}$ low, OCH_2Me), 21.66 (s, ArMe), 33.48 (s, 3-Me), 41.48 (s, NMe), 60.28 (d, $J_{P,C}$ 161, C-5), 65.33 (s, C-4), 60.37 (s, OCH_2), 129.49 (s), 129.73 (s), 131.39 (s), 145.94 (s), and 153.35 (s, C-2); *m/z* (d.c.i., NH_3) 421 (M^+ + 1, 100).

Diethyl 2-Amino-4-p-tolylsulphonyl-4,5-dihydrothiazol-5-ylphosphonate (**26**).—The acetylene (**12**) (1.0 g) and thiourea (0.25 g) were stirred in ethanol (5 ml) for 5 min, after which most of the solvent was evaporated off and the excess of thiourea precipitated with chloroform. All the solvent was now evaporated and the residue chromatographed, eluting with methanol–ether (1:9, v/v) to give the *thiazole* (**26**) as a colourless powder, m.p. 187.5—189 °C (Found: C, 43.1; H, 5.2; N, 6.8. $C_{14}H_{21}N_2O_5PS_2$ requires C, 42.9; H, 5.4; N, 7.1%); $\nu_{max.}$ 1 660, 1 640, and 1 639 cm^{-1}; δ_H($CDCl_3$ + CD_3OD) 1.28 (6 H, t, *J* 7, 2 × CH_2Me), 2.43 (3 H, s, 4-Me), 3.65 (2 H, br s, NH_2), 4.09 (4 H, 5 lines, *J* 7, 2 × OCH_2), 5.05 (2 H, approx. t, *J ca.* 16, 4,5-H_2), 7.36 (2 H, d, *J* 8, ArH_2), and 7.82 (2 H, d, *J* 8, ArH_2); δ_C 15.84 (d, $J_{P,C}$ 5, CH_2Me), 21.24 (s, 4-Me), 63.37 (d, $J_{P,C}$ 7, OCH_2), 69.51 (d, $J_{P,C}$ 160, C-5), 73.95 (s, C-4), 129.52 (s), 129.60 (s), 131.63 (s), 145.73 (s), and 161.16 (d, *J* 7, C-2); *m/z* (i.b.e.i.) 255 (14), and 237 (100); *m/z* (d.c.i., NH_3) 408 (M^+ + NH_2, 100).

3-Cyanoindolizines and 3-Cyanopyrrolo[2,1-a]*isoquinoline from Pyridinium- or Isoquinolinium-2-dicyanomethylide and Acetylenes.*—The acetylene and the dicyanomethylide [26] (1 mol equiv.) were refluxed in toluene (5—10 ml) for the stated time. Column chromatography of the products and eluting with ether (A), or methanol–ether (1:9, v/v, B), gave the indolizine.

Indolizines from pyridinium-1-dicyanomethylide. (i) Diethyl *p*-tolylthioethynylphosphonate (**10**) (1.0 g; 15 h) gave the *indolizine* (**30**), as white needles (0.7 g) (from cyclohexane), m.p. 85—86 °C (Found: C, 60.0; H, 5.3; N, 7.0. $C_{20}H_{21}N_2O_3PS$ requires C, 60.0; H, 5.3; N, 7.0%); $\nu_{max.}$ 2 210, 1 630, and 1 490 cm^{-1}; δ_H 1.30 (6 H, t, *J* 7, 2 × CH_2Me), 2.30 (3 H, s, 4-Me), 4.12 (4 H, 5 lines, *J* 7, 2 × OCH_2), 6.81—7.48 (6 H, m, ArH_6), and 8.15—8.44 (2 H, m, ArH_2); δ_C 16.13 (d, $J_{P,C}$ 7, CH_2Me), 21.03 (s, 4-Me), 61.96 (d, $J_{P,C}$ 5, OCH_2), 100.60 (d, $J_{P,C}$ 15, C-3), 101.10 (d, $J_{P,C}$ 230, C-1), 111.27 (s, CN-3), 114.67 (s), 120.05 (s), 124.87 (s), 125.47 (s), 127.22 (s), 129.52 (d, $J_{P,C}$ 11, C-2), 129.78 (s), 132.25 (s), 138.25 (s), and 140.60 (d, $J_{P,C}$ 25, C-8a); *m/z* (d.c.i., NH_3) 401 (M^+ + 1, 100) and 400 (M^+, 20).

(ii) Diethyl *p*-tolylsulphinylethynylphosphonate (**11**) (1.0 g) (1 h, A) gave *diethyl 3-cyano-2-p-tolylsulphinylindolizin-1-ylphosphonate* (**31**), as yellow prisms (0.47 g) (from cyclohexane–toluene), m.p. 158—160 °C (Found: C, 57.7; H, 5.0; N, 6.8. $C_{20}H_{21}N_2O_4PS$ requires C, 57.7; H, 5.1; N, 6.8%); $\nu_{max.}$ 2 210, 1 630, 1 595, 1 490, and 1 470 cm^{-1}; δ_H 1.30 (6 H, t, *J* 7, 2 × CH_2Me), 2.33 (3 H, s, 4-Me), 3.90—4.57 (4 H, m, 2 × OCH_2), 6.95—7.45 (4 H, m, ArH_4), 7.93 (2 H, d, *J* 8, ArH_2), and 8.09—8.45 (2 H, m, ArH_2); δ_C 16.22 (d, $J_{P,C}$ 6.4, CH_2Me), 21.34 (s, 4-Me), 62.37 (d, $J_{P,C}$ 4, OCH_2), 110.57 (s, CN-3), 115.90 (s), 120.45 (s), 125.26 (s), 125.34 (s), 126.23 (s), and 129.76 (s), all resonances not observable; *m/z* (d.c.i., NH_3) 417 (M^+ + 1, 100), 401 (57), and 279 (17).

(iii) Diethyl 2-*p*-tolylsulphonyl-1-ethynylphosphonate (**12**) (0.55 g) (45 min, A) gave the *diethyl 3-cyano-1-p-tolylsulphonylindolizin-2-ylphosphonate* (**33**), as white needles (0.108 g) [from dichloromethane–light petroleum (b.p. 80—100 °C)], m.p. 179—180 °C (Found: C, 55.2; H, 5.1; N, 6.3. $C_{20}H_{21}N_2O_5PS$ requires C, 55.5; H, 4.9; N, 6.5%); $\nu_{max.}$ 2 225, 1 635, and 1 600 cm^{-1}; δ_H 1.42 (6 H, t, *J* 7, 2 × CH_2Me), 2.33 (3 H, s, 4-Me), 4.35 (4 H, 5 lines, *J* 7, 2 × OCH_2), 7.00—7.59 (4 H, m, ArH_4), 8.14 (2 H, d, *J* 8, ArH_2), and 8.32—8.55 (2 H, m, ArH_2); δ_C 16.23 (d, $J_{P,C}$ 6, CH_2Me), 21.51 (s, Me), 63.62 (d, $J_{P,C}$ 7, OCH_2), 103.13 (d, $J_{P,C}$ 12, C-3), 111.29 (s, CN-3), 116.63 (d, $J_{P,C}$ 9, C-1), 116.41 (s), 119.88 (s), 123.96 (d, $J_{P,C}$ 208, C-2), 125.52 (s), 127.41 (s), 127.49 (s), 129.49 (s), 137.03 (d, $J_{P,C}$ 13, C-8a), 139.73 (s), and 143.94 (s); *m/z* (d.c.i., NH_3) 433 (M^+ + 1, 100), 432 (M^+, 15), and 367 (20).

(iv) Ethynyl *p*-tolyl sulphone (0.17 g) (2 h, B) gave *3-cyano-1-p-tolylsulphonylindolizine* (**34**), as yellow prisms (0.13 g) [from dichloromethane–light petroleum (b.p. 80—100 °C)], m.p. 176—177 °C (Found: C, 65.1; H, 4.2; N, 9.6. $C_{16}H_{12}N_2O_2S$ requires C, 64.9; H, 4.1; N, 9.5%); $\nu_{max.}$ 2 115, 1 635, and 1 505 cm^{-1}; δ_H 2.35 (3 H, s, Me), 6.92—7.52 (4 H, m, ArH_4), 7.70 (1 H, s, 2H), 7.87 (2 H, d, *J* 8, ArH_2), and 8.10—8.40 (2 H, m, ArH_2); δ_C 21.39 (s, Me), 97.26 (s, C-3), 111.59 (s, CN-3), 114.40 (s, C-1), 115.49 (s), 118.56 (s), 123.67 (s, C-2), 125.78 (s), 126.46 (s), 126.62 (s), 129.78 (s), 134.96 (s, C-8a), 139.96 (s), and 143.84 (s); *m/z* (d.c.i., NH_3) 314 (M^+ + 18, 100), 297 (M^+ + 1, 30), and 296 (M^+, 20).

(v) Diethyl chloroethynylphosphonate (**8**) (0.5 g) (2 h, A) gave *diethyl 2-chloro-3-cyanoindolizin-1-ylphosphonate* (**35**) as large colourless plates (0.32 g) (from cyclohexane–toluene), m.p. 82—83.5 °C (Found: C, 50.1; H, 4.7; N, 9.1. $C_{13}H_{14}ClN_2O_3P$ requires C, 49.9; H, 4.5; N, 9.0%); $\nu_{max.}$ 2 200 cm^{-1}; δ_H 1.36 (6 H, t, *J* 7, 2 × CH_2Me), 4.15 (4 H, 5 lines, *J* 7, 2 × OCH_2), 6.94—7.39 (2 H, m, ArH_2), and 8.21—8.37 (2 H, m, ArH_2); *m/z* (i.b.e.i.) 314 + 312 (M^+, 15 + 43), 277 (9), 258 + 256 (4 + 11), 238 (11), 193 + 191 (5 + 23), 178 + 176 (18 + 54), and 169 (100).

Pyrrolo[2,1-a]*isoquinolines from 2-isoquinolinium-2-dicyanomethylide.* (i) Diethyl ethynylphosphonate (**7**) (2.34 g) (7 h, A) gave *diethyl 3-cyanopyrrolo*[2,1-a]*isoquinolin-1-ylphosphonate* (**36**), as cream plates (2.92 g) [from cyclohexane–toluene, 1:1 (v/v)], m.p. 123.5—125 °C (Found: C, 61.8; H, 5.3; N, 8.3. $C_{17}H_{17}N_2O_3P$ requires C, 62.2; H, 5.2; N, 8.5%); $\nu_{max.}$ 2 220, 1 550, 1 245, 1 230, 1 220, 1 050, 1 025, and 980 cm^{-1}; δ_H 1.33 (6 H, t, *J* 7, 2 × CH_2Me), 4.10 (4 H, 5 lines, *J* 7, 2 × OCH_2), 7.16 (1 H, d, $J_{P,H}$ 7, 9-H), 7.60—7.79 (4 H, m, ArH_4), 8.14 (1 H, dd, *J* 7 + 2, 10-H), and 9.00—9.20 (1 H, m, ArH); *m/z* 328 (M^+, 100), 300 (15), 272 (15), 254 (20), 237 (15), 207 (25), and 192 (100).

Iodotrimethylsilane (1.8 ml) [27] was injected into a stirred suspension of the ester (**36**) (2.0 g) in tetrachloromethane (30 ml) under nitrogen at −10 °C and the mixture stored overnight in order to reach room temperature. The solvent was removed, methanol added (20 ml), and this then also removed. Trituration with chloroform gave the acid (**39**) (1.66 g) as a pale green powder, which was not obtained analytically pure, *m/z* (i.b.e.i.) 192 (M^+ − HPO_3, 100), *m/z* (d.c.i., NH_3), 193 (100); *m/z* (f.a.b., Ar^+) 273 (M^+, 100).

This acid (0.1 g) was refluxed in methanol (4 ml) and concentrated aqueous hydrochloric acid (0.2 ml) for 10 h. The solvent was evaporated off from the clear blue solution. The residue was treated with saturated aqueous sodium hydrogencarbonate and chloroform now extracted 3-cyanopyrrolo[2,1-*a*]isoquinoline (25 mg), a pale green powder (from hexane) with the described properties. [28]

(ii) Ethynyl *p*-tolyl sulphone (**4**) (0.2 g) (2.5 h, A) gave *3-cyano-1-p-tolylsulphonylpyrrolo*[2,1-a]*isoquinoline* (**37**), off-white prisms (0.25 g) [from dichloromethane–light petroleum (b.p. 80—100 °C)], m.p. 236—238 °C (Found: C, 69.2; H, 4.2; N, 7.9. $C_{20}H_{14}N_2O_2S$ requires C, 69.4; H, 4.1; N, 8.1%); $\nu_{max.}$ 2 225, 1 525, 1 500, 1 380, 1 350, 1 340, 1 305, 1 145, 1 105, 1 080, and 790 cm^{-1}; δ_H 2.33 (3 H, s, 4-Me), 7.19—7.32 (3 H, m, ArH_3), 7.62—7.92 (6 H, m, ArH_6), 8.10 (1 H, d, *J* 7, 10-H), and 9.00—9.30 (1 H, m, ArH); *m/z* (d.c.i., NH_3) 364 (M^+ + 18, 34), 347 (M^+ + 1, 100), 346 (M^+, 25), 193 (65), and 192 (15).

(iii) *Tetraethyl 3-cyanopyrrolo*[2,1-a]*isoquinoline-1,2-diyldiphosphonate* (**38**) was obtained from the ester (**9**) (1.0 g) (5 h,

B) as *pale pink needles* (0.85 g) (from cyclohexane–toluene), m.p. 120—121 °C (Found: C, 54.2; H, 5.7; N, 6.0. $C_{21}H_{26}N_2O_6P_2$ requires C, 54.3; H, 5.6; N, 6.0%); $\nu_{max.}$ 2 220 cm^{-1}; δ_H 1.30 (6 H, t, *J* 7, 2 × CH_2Me), 1.42 (6 H, t, *J* 7, 2 × CH_2Me), 3.98—4.55 (8 H, m, 4 × OCH_2), 7.30 (1 H, d, *J* 7, 9-H), 7.56—7.80 (3 H, m, ArH_3), 8.21 (1 H, dd, *J* 7 + 2, 10-H), and 9.20—9.40 (1 H, m, ArH); *m/z* (i.b.e.i.) 463 ($M^+ - 1$, 89), 354 (76), 334 (47), 326 (100), 316 (29), and 299 (35).

(iv) *Diethyl 3-cyano-2-p-tolylsulphonylpyrrolo*[2,1-a]*isoquinolin-1-ylphosphonate* (**41**), containing the isomer (**42**), was obtained from the ester (**12**) (0.31 g) (1h, A) as a *pale yellow powder* (**41**) (0.19 g) (from cyclohexane–toluene), m.p. 171—179 °C (Found: C, 59.5; H, 4.9; N, 6.1. $C_{24}H_{23}N_2O_5PS$ requires C, 59.5; H, 4.8; N, 5.8%); $\nu_{max.}$ 2 225 cm^{-1}; δ_H 1.15 (4 H, t, *J* 7), 1.46 (2 H, t, *J* 7), 2.31 (1 H, s), 2.39 (2 H, s), 3.75—4.67 (4 H, m), 7.20—7.41 (3 H, m), 7.65—7.78 (3 H, m), 7.98—8.30 (3 H, m), and 9.15—9.30 (1 H, m); *m/z* (i.b.e.i.) 482 (M^+, 24), 417 (100), 390 (29), 361 (33), and 300 (40).

The above pyrrolo[2,1-*a*]isoquinoline (0.12 g) was treated with iodotrimethylsilane followed by methanolic hydrochloric acid, as for (**36**), and at this point cooling and filtration gave 3-*cyano*-2-p-*tolylsulphonylpyrrolo*[2,1-a]*isoquinoline* (**43**) as a yellow powder ('insoluble' in chloroform, dimethyl sulphoxide, water, and methanol), m.p. 277—279 °C (Found: C, 68.5; H, 3.9; N, 8.0. $C_{20}H_{14}N_2O_2S{\cdot}0.2H_2O$ requires C, 68.6; H, 4.1; N, 8.0%); *m/z* (f.a.b., Ar^+) 347 (M^+, 100%).

Diethyl 3-Cyano-2-p-tolylsulphonylindolizin-1-ylphosphonate (**32**).—(i) The arylthioindolizine (**30**) (0.4 g) and 3-chloroperbenzoic acid (0.41 g) were stirred in chloroform (10 ml) at 0 °C and the mixture allowed to attain room temperature overnight. The mixture was washed with saturated aqueous sodium sulphite (2 × 25 ml), saturated aqueous sodium hydrogencarbonate (2 × 25 ml), and water, dried, and evaporated to give the *indolizine* (**32**) as colourless prisms (0.3 g) (from cyclohexane), m.p. 130—137.5 °C (Found: C, 55.4; H, 4.9; N, 6.4. $C_{20}H_{21}N_2O_5PS$ requires C, 55.6; H, 4.9; N, 6.5%); $\nu_{max.}$ 2 115, 1 630, 1 595, 1 490, 1 340, 1 230, 1 185, 1 175, 1 155, 1 015, 990, 980, and 935 cm^{-1}; δ_H 1.30 (6 H, t, *J* 7, CH_2Me), 2.40 (3 H, s, 4-Me), 4.12 (4 H, 5 lines, *J* 7, 2 × OCH_2), 7.05—7.50 (4 H, m, ArH_4), 8.13 (2 H, d, *J* 8, ArH_2), and 8.35—8.70 (2 H, m, ArH_2); δ_C 16.15 (d, $J_{P,C}$ 7, CH_2Me), 21.57 (s, 4-Me), 62.58 (d, $J_{P,C}$ 5, OCH_2), 100.23 (d, $J_{P,C}$ 218, C-1), 101.30 (d, $J_{P,C}$ 15, C-3), 110.48 (s, CN-3), 116.75 (s), 122.32 (s), 125.28 (s), 126.49 (s), 127.43 (s, C-2?), 128.47 (s), 129.52 (s), 138.12 (s), 140.59 (d, $J_{P,C}$ 23, C-8a), and 144.95 (s); *m/z* (d.c.i., NH_3) 433 (M^+ + 1, 100) and 279 (75).

(ii) The sulphoxide (**31**) (200 mg) was treated as for the thioether (**30**) above and gave the same sulphone (90 mg), identical in properties with the analysed sample.

Diethyl p-Tolylsulphonylethynylphosphonate (**12**) *with Dienes*.—(i) This ester (0.5 g) was stirred with cyclohexa-1,3-diene (0.2 ml) in dry ether (2 ml) for 20 h after which the mixture was evaporated and the residue chromatographed with ether as eluant to give *diethyl* 3-p-*tolylsulphonylbicyclo*[2.2.2]*octa-2,5-dien-2-ylphosphonate* (**44**) as large off-white prisms (0.273 g) [from dichloromethane–light petroleum (b.p. 80—100 °C)], m.p. 72—78 °C (Found: C, 57.4; H, 6.3. $C_{19}H_{25}O_5PS$ requires C, 57.6; H, 6.3%); δ_H 1.26—1.49 [10 H, m, $(CH_2)_2$ + 2 × CH_2Me], 2.41 (3 H, s, 4-Me), 4.00—4.60 (6 H, m, 1,4-H_2 + 2 × OCH_2), 6.21—6.39 (2 H, m, 5,6-H_2), 7.31 (2 H, d, *J* 8, ArH_2), and 8.00 (2 H, d, *J* 8, ArH_2); *m/z* (d.c.i., NH_3) 397 (M^+ + 1, 100) and 369 (18).

(ii) The ester (**12**) (0.5 g) and furan (0.17 ml) were stirred in dry ether (2 ml) for 20 h after which the mixture was evaporated and the residue chromatographed as above to give diethyl 3-*p*-tolylsulphonyl-1,4-epoxycyclohexa-2,5-dien-2-ylphosphonate (**45**), as a colourless oil (0.42 g) which darkened on contact with air and was characterised spectroscopically; δ_H 1.34 (6 H, t, *J* 7, 2 × CH_2Me), 2.40 (3 H, s, ArMe), 4.19 (4 H, 5 lines, *J* 7, 2 × OCH_2), 5.51 (1 H, br s, 1- or 4-H), 5.78 (1 H, br s, 4- or 1-H), 6.80—7.04 (2 H, m, 5,6-H_2), 7.29 (2 H, d, *J* 8, ArH_2), and 7.81 (2 H, d, *J* 8, ArH_2); *m/z* (d.c.i., NH_3) 402 (M^+ + 18, 30), 385 (M^+ + 1, 100), 334 (92), 317 (23); (i.b.e.i.) 316 (52), 288 (18), and 260 (100).

(iii) The acetylene (**12**) (0.5 g) and 1-acetoxybuta-1,3-diene (0.28 ml) were stirred in dry ether (2 ml) for 60 h and chromatography as above gave *diethyl* 2-p-*tolylsulphonylphenylphosphonate* (0.4 g) as colourless needles (from cyclohexane), m.p. 87—89 °C (Found: C, 55.3; H, 5.8. $C_{17}H_{21}O_5PS$ requires C, 55.4; H, 5.7%); δ_H 1.32 (6 H, t, *J* 7, 2 × CH_2Me), 2.34 (3 H, s, 4-Me), 4.20 (4 H, 5 lines, *J* 7, 2 × OCH_2), and 7.20—7.80 (8 H, m, ArH_8); *m/z* (d.c.i., NH_3) 369 (M^+ + 1, 100) and 303 (14).

Ethanoanthracenes.—The appropriate acetylene and the anthracene were refluxed for the stated time in the solvent (a few ml) indicated, the solvent evaporated off and the residue chromatographed over silica and eluted with ether (A) or methanol–ether (1:9, v/v, B).

(i) The acetylene (**7**) (2.0 g) and anthracene (2.19 g) (10.5 h, xylene, B) gave *diethyl* 9,10-*dihydro*-9,10-*ethenoanthracen*-11-*ylphosphonate* (**46**), as white prisms (1.08 g) (from cyclohexane), m.p. 67—71 °C (Found: C, 70.6; H, 6.2. $C_{20}H_{21}O_3P$ requires C, 70.6; H, 6.2%); δ_H (300 MHz) 1.22 (6 H, t, *J* 7, CH_2Me), 3.75—3.88 (2 H, m, OCH_2), 3.88—4.02 (2 H, m, OCH_2), 5.31 (1 H, dd, $J_{9,12}$ 6, $J_{H,P}$ 4, 9-H), 5.38 (1 H, dd, $J_{H,P}$ 9, $J_{10,12}$ 1, 10-H), 6.95—7.02 (4 H, m), 7.27—7.37 (4 H, m), 7.83 (1 H, ddd, $J_{P,H}$ 15, $J_{9,12}$ 6, $J_{10,12}$ 1, 12-H; collapses to d, *J* 15 on strong irradiation at δ 5.32 at 60 MHz); δ_C 16.04 (d, $J_{P,C}$ 7, CH_2Me), 51.59 (d, $J_{P,C}$ 11, C-9- or -10), 51.87 (d, $J_{P,C}$ 14, C-9 or -10), 61.65 (d, $J_{P,C}$ 4, OCH_2), 123.09 (s), 123.32 (s), 124.77 (s), 140.66 (d, $J_{P,C}$ 193, C-11), 144.05 (s), 144.50 (s), and 154.41 (d, $J_{P,C}$ 13, C-12); *m/z* (d.c.i., NH_3) 341 (M^+ + 1, 46), 340 (M^+, 23), 202 (100), and 178 (17).

(ii) The ester (**7**) (1.0 g) and 9-methylanthracene (1.0 g) (7 h, xylene, A) gave *diethyl* 9-*methyl*-9,10-*dihydro*-9,10-*ethenoanthracen*-11-*ylphosphonate* (**47**) as small white prisms (0.27 g) (from light petroleum), m.p. 95.5—97 °C (Found: C, 71.4; H, 6.6. $C_{21}H_{23}O_3P$ requires C, 72.1; H, 6.5%); δ_H 1.19 (6 H, t, *J* 7), 2.20 (3 H, s), 3.70—4.16 (4 H, m), 5.31 (1 H, dd, *J* 9 + 1), 6.90—7.61 (8.5 H, m), and 7.70 (0.5 H, d, *J* 1); *m/z* (d.c.i., NH_3) 355 (M^+ + 1, 100) and 216 (50).

A second fraction from the column consisted of a mixture of (**47**) and the 12-phosphonate isomer (**48**) in the ratio 2:1 respectively, as a pale yellow oil (0.63 g) δ_H as above, with extra peaks at 2.39 (1 H, s), 5.15—5.40 (m), and 8.01 (0.3 H, dd, *J* 15 + 6).

(iii) The ester (**9**) (2.0 g) and anthracene (1.2 g) (24 h, toluene, B) gave *tetraethyl* 9,10-*dihydro*-9,10-*ethenoanthracene*-11,12-*diyldiphosphonate* (**49**) as a colourless oil (1.69 g) which was spectroscopically pure, δ_H 1.20 (12 H, t), 3.74—4.44 (8 H, m), 5.80 (2 H, t, *J* 6), 6.88—7.10 (4 H, m), and 7.21—7.43 (4 H, m); δ_C 16.01 (t, $J_{P,C}$ 3, CH_2Me), 55.36 (t, $J_{P,C}$ 11, C-9, -10), 62.24 (s), 123.46 (s), 125.11 (s), 143.19 (s), and 152.00 (dd, $J_{P,C}$ 192 + 11, C-11, -12); *m/z* (d.c.i., NH_3) 477 (M^+ + 1, 100), 316 (60), 178 (47), and 139 (24).

(iv) The ester (**9**) (0.5 g) and 9-methylanthracene (0.32 g) (24 h, toluene, B) gave the spectroscopically pure adduct (**50**) as a colourless oil (0.27 g), δ_H 1.18 (6 H, t, *J* 7, 2 × CH_2Me), 1.22 (6 H, t, *J* 7, 2 × CH_2Me), 2.50 (3 H, s, 9-Me), 3.90 (4 H, 5 lines, *J* 7, 2 × OCH_2), 4.01 (4 H, 5 lines, *J* 7, 2 × OCH_2), 5.95 (1 H, dd, $J_{P,H}$ 9 + 5, 10-H), 6.90—7.05 (4 H, m, ArH_4), and 7.29—7.43 (4 H, m, ArH_4); δ_C 14.60 (s), 16.06 (t, $J_{P,C}$ 6, CH_2Me), 53.69 (t, $J_{P,C}$ 12, C-9), 55.74 (dd, $J_{P,C}$ 13 + 10, C-10), 62.20 (t, $J_{P,C}$ 7, OCH_2), 121.39 (s), 123.31 (s), 124.97 (s), 144.25 (s), 145.96 (s), 153.60 (dd, $J_{P,C}$ 180 + 13, C-11 or -12), and 156.70 (dd, $J_{P,C}$ 186 + 15,

C-12 or -11); *m/z* (c.i., NH_3) 491 ($M^+ + 1$, 47), 355 (32), 193 (100), 192 (36), and 139 (63).

(v) The ester (**12**) (1.5 g) and anthracene (0.84 g) (1 h, toluene, A) gave *diethyl* 12-p-*tolylsulphonyl*-9,10-*dihydro*-9,10-*ethenoanthracen*-11-*ylphosphonate* (**51**) (1.92 g) as prisms (from ether), m.p. 146—148 °C (Found: C, 65.6; H, 5.6. $C_{27}H_{27}O_5PS$ requires C, 65.6; H, 5.5%); δ_H 1.23 (6 H, t, *J* 7, 2 × CH_2Me), 2.34 (3 H, s, ArMe), 4.05 (4 H, 5 lines, *J* 7, 2 × OCH_2), 5.60 (1 H, d, *J* 5, 9-H), 5.82 (1 H, d, *J* 9, 10-H), 6.85—7.42 (10 H, m, ArH_{10}), and 7.83 (2 H, d, *J* 8, ArH_2); δ_C 16.12 (d, $J_{P,C}$ 6, CH_2Me), 21.49 (s, ArMe), 54.30 (d, $J_{P,C}$ 10, C-9 or -10), 56.00 (d, $J_{P,C}$ 8, C-10 or -9), 62.84 (d, $J_{P,C}$ 6, OCH_2), 123.50 (s), 123.67 (s), 125.40 (s), 125.49 (s), 128.26 (s), 129.50 (s), 136.39 (s), 142.63 (s), 142.88 (s), 144.65 (s), 147.72 (d, $J_{P,C}$ 189, C-11), and 161.60 (d, $J_{P,C}$ 8, C-12); *m/z* (i.b.e.i.) 494 (M^+, 1), 429 (74), 339 (35), 202 (64), and 178 (100).

(vi) The ester (**12**) (0.5 g) and 9-methylanthracene (0.45 g) (48 h, ether, room temperature, scratching, and filtration) gave *diethyl* 9-*methyl*-11-p-*tolylsulphonyl*-9,10-*dihydro*-9,10-*ethenoanthracen*-12-*ylphosphonate* (**52**) as white prisms (0.25 g) [from dichloromethane–light petroleum, (b.p. 80—100 °C)], m.p. 162.5—164.5 °C (Found: C, 66.2; H, 5.8. $C_{28}H_{29}O_5PS$ requires C, 66.1; N, 5.7%); δ_H 1.04 (6 H, t, *J* 7, 2 × CH_2Me), 2.30 (3 H, s, Me), 2.44 (3 H, s, Me), 3.71 (4 H, 5 lines, *J* 7, 2 × OCH_2), 6.05 (1 H, d, *J* 5, 10-H), and 6.94—7.63 (12 H, m, ArH_{12}); δ_C 15.03 (s, Me-9), 15.95 (d, $J_{P,C}$ 7, CH_2Me), 21.42 (s, ArMe), 54.06 (d, $J_{P,C}$ 11, C-10), 54.53 (d, $J_{P,C}$ 10, C-9), 62.37 (d, $J_{P,C}$ 5, OCH_2), 121.68 (s), 123.63 (s), 125.36 (s), 127.34 (s), 128.85 (s), 138.78 (s), 143.72 (s), 145.85 (s), 148.85 (d, $J_{P,C}$ 180, C-12), and 166.83 (d, $J_{P,C}$ 9, C-11); *m/z* (d.c.i., NH_3) 509 ($M^+ + 1$, 100), 444 (16), 353 (33), 215 (25), and 192 (39).

(vii) The ester (**11**) (0.55 g), and 9-methylanthracene (0.35 g) (3 h, toluene, A) gave *diethyl* 9-*methyl*-11-(p-*tolylsulphinyl*)-9,10-*dihydro*-9,10-*ethenoanthracen*-12-*ylphosphonate* (**53**), as small white prisms (0.3 g) (from cyclohexane–toluene), m.p. 164—176 °C (Found: C, 68.2; H, 5.9. $C_{28}H_{29}O_4PS$ requires C, 68.3; H, 5.9%); δ_H 1.08 (3 H, t, *J* 7, 2 × CH_2Me), 1.17 (3 H, t, *J* 7, 2 × CH_2Me), 2.24 (3 H, s, 9-Me), 2.36 (3 H, s, ArMe), 3.50—4.20 (4 H, m, 2 × OCH_2), 6.04 (1 H, d, *J* 5, 10-H), 6.76—7.51 (10 H, m, ArH_{10}), and 7.61 (2 H, d, *J* 9, ArH_2); *m/z* (d.c.i., NH_3) 493 ($M^+ + 1$, 100), 477 (17), and 355 (15).

This compound (64 mg) was oxidised as for the sulphide (**54**), below, and gave the sulphone (**52**) (31 mg), with identical m.p., mixed m.p. and spectra to the analysed sample; mixed m.p. with the isomer (**55**) 137—143 °C.

(viii) The ester (**10**) (1.0 g) and 9-methylanthracene (0.67 g) (9 h, 160 °C without solvent, A) gave spectroscopically pure diethyl 9-methyl-12-*p*-tolylthio-9,10-dihydro-9,10-ethenoanthracen-11-ylphosphonate (**54**) as a colourless oil (0.75 g), δ_H 1.13 (6 H, t, *J* 7, 2 × CH_2Me), 1.99 (3 H, s, 9-Me), 2.22 (3 H, s, ArMe), 3.94 (4 H, 5 lines, *J* 7, 2 × OCH_2), 5.74 (1 H, d, *J* 10, 10-H), and 6.62—7.48 (12 H, m, ArH_{12}); δ_C 13.77 (s, Me-9), 16.07 (d, $J_{P,C}$ 7, CH_2Me), 20.81 (s, ArMe), 54.31 (d, $J_{P,C}$ 10, C-10), 57.08 (d, $J_{P,C}$ 12, C-9), 62.00 (d, $J_{P,C}$ 5, OCH_2), 120.90 (s), 123.02 (s), 124.72 (s), 125.08 (s), 127.96 (s), 129.50 (s), 132.36 (s), 135.67 (s), 144.40 (d, *J* 3), 146.60 (s), 148.57 (d, $J_{P,C}$ 194, C-11), and 159.10 (d, $J_{P,C}$ 7, C-12); *m/z* (d.c.i., NH_3) 477 ($M^+ + 1$, 100) and 192 (80).

This compound (**54**) (0.44 g) and 3-chloroperbenzoic acid (0.36 g) were stirred in chloroform (5 ml) at 0 °C for 1 h and then at room temperature for 17 h. The mixture was washed with saturated aqueous sodium sulphite (2 × 20 ml) and saturated aqueous sodium hydrogencarbonate (2 × 20 ml), dried, and evaporated and the residue triturated with ether (3 ml) to give *diethyl* 9-*methyl*-12-p-*tolylsulphonyl*-9,10-*dihydro*-9,10-*ethenoanthracen*-11-*ylphosphonate* (**55**) as small white needles (0.14 g) (from cyclohexane), m.p. 175—176.5 °C (Found: C, 66.2; H, 5.8. $C_{28}H_{29}O_5PS$ requires C, 66.1; H, 5.7%); δ_H 1.29 (6 H, t, *J* 7, 2 × CH_2Me), 2.15 (3 H, s, 9-Me), 2.29 (3 H, s, ArMe), 4.17 (4 H, 5 lines, *J* 7, 2 × OCH_2), 6.03 (1 H, d, *J* 9, 10-H), 6.86—7.45 (10 H, m, ArH_{10}), and 7.66 (2 H, d, *J* 8, ArH_2); δ_C 13.71 (s, 9-Me), 16.25 (d, $J_{P,C}$ 7, CH_2Me), 21.51 (s, ArMe), 52.94 (d, $J_{P,C}$ 11, C-10), 56.03 (d, $J_{P,C}$ 7, C-9), 62.99 (d, $J_{P,C}$ 6, OCH_2), 121.44 (s), 123.56 (s), 125.22 (s), 125.34 (s), 127.23 (s), 129.52 (s), 137.66 (s), 143.64 (d, *J* 3), 144.14 (s), 145.45 (s), 154.16 (d, $J_{P,C}$ 189, C-11), and 161.20 (d, $J_{P,C}$ 5, C-12); *m/z* (i.b.e.i.) 508 (M^+, 2), 444 (11), 353 (25), 215 (28), and 192 (100).

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