X-ray structures of adducts of 1,2,5-triphenylphosphole with dimethyl acetylenedicarboxylate: a confirmation, a revision, and a new structure¹

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Dimethyl acetylenedicarboxylate was reacted with 1,2,5-triphenylphosphole under mild conditions, and four products isolated. Regardless of conditions used, every preparation gave low yields of dimethyl 3,6-diphenylphthalate coincident with loss of the phosphorus bridge. NMR data and X-ray crystal structures are provided for a yellow, and a red, 2:1 adduct. The yellow adduct, tetramethyl 1,6,7-triphenyl-6-phospha(V)-tricyclo[7.3.1.0^{1,9}]nona-3,5,7-triene-2,3,4,5tetracarboxylate 6, crystallized in the triclinic space group P1 (No. 2) with two molecules in the unit cell. Refinement $(a = 11.259(1) \text{ Å}, b = 12.947(3) \text{ Å}, c = 13.784(3) \text{ Å}, \alpha = 112.25(2)^\circ, \beta = 103.44(1)^\circ, \text{ and } \gamma = 101.80(1)^\circ) \text{ con$ verged at R = 0.0453 ($R_w = 0.0453$) for 537 parameters using 2880 reflections with $I > 2\sigma(I)$. The red adduct, trimethyl 1,2,5-triphenylphosphoranylidene-4-methoxycyclopent-2-ene-5-one-2,3,4-tricarboxylate, an exocyclic phosphorane 8, crystallized in the monoclinic space group $P2_1/c$ (No. 14) with four molecules in the unit cell. Refinement of this structure (a = 13.233(5) Å, b = 15.712(5) Å, c = 17.191(7) Å, $\alpha = 90^{\circ}$, $\beta = 110.35(4)^{\circ}$, and $\gamma = 90^{\circ}$) converged at R = 0.0916 ($R_w = 0.0937$) for 400 parameters using 2052 reflections with $I > 2.5\sigma(I)$. Small amounts of a white or buff amorphous material, which could represent a polymeric product from the lost phosphorus bridge, were also obtained. Thermal rearrangement of the yellow adduct gave a colourless 6,5,3 tricyclic isomer 11, possibly via the isomeric cyclopropyl derivative 15 or the nine-membered phosphonin 7. The structure of 11 was confirmed by mild oxidation of the colourless rearrangement product to its P-oxide. This product, tetramethyl 2,3,6-triphenyl-2-phosphatricy $clo[6.1.0^{1.8}.0^{5.9}]$ -2-oxonona-3,6-diene-1,7,8,9-tetracarboxylate 12, was also colourless. It crystallized in the orthorhombic space group $Pbc2_1$ (No. 29) with four pairs of molecules in the unit cell. Refinement of this structure (a = 8.918(1)Å, b = 22.605(4) Å, and c = 30.169(6) Å) converged at R = 0.0747 ($R_w = 0.0757$) for 321 parameters using 3255 reflections with $I \ge 3\sigma(I)$. Unequivocal structures for these adducts and derivatives finally confirms, and establishes further understanding of, the complex reactions of the triphenylphosphole with dimethyl acetylenedicarboxylate.

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On a fait réagir l'acétylènedicarboxylate de diméthyle avec le 1,2,5-triphénylphosphole dans des conditions douces et on a isolé quatre produits. Quelles que soient les conditions utilisées, chaque préparation a conduit à de faibles rendements de 3,6-diphénylphtalate de diméthyle qui résulte de la perte du pont phosphoré. On rapporte les données RMN et les structures cristallines déterminées par diffraction des rayons X d'un adduit jaune et d'un adduit 2 : 1 qui est rouge. Les cristaux de l'adduit jaune, le 1,6,7-triphényl-6-phospha(V)-tricyclo[7.3.1.0^{1,9}]nona-3,5,7-triène-2,3,4,5-tétracarboxylate de tétraméthyle; 6, sont tricliniques, groupe d'espace PI (No. 2) avec a = 11,259(1), b = 12,947(3) et c =13,784(3) Å, $\alpha = 112,25(2)^{\circ}$, $\beta = 103,44(1)^{\circ}$ et $\gamma = 101,80(1)^{\circ}$ et deux molécules par motif. L'affinement de 537 paramètres provenant de 2880 réflexions avec $I > 2\sigma(I)$ converge à R = 0.0453 ($R_w = 0.0453$). Les cristaux de l'adduit rouge, le phosphorane exocyclique 8, le 1,2,5-triphénylphosphoranylidène-4-méthoxycyclopent-2-èn-5-one-2,3,4-tricarboxylate de triméthyle, sont monocliniques, groupe d'espace P_{2_1}/c (No. 14) avec a = 13,233(5), b = 15,712(5) et c = 17,191(7) Å, $\alpha = 90^{\circ}, \beta = 110,35(4)^{\circ}$ et $\gamma = 90^{\circ}$ et quatre molécules par motif. L'affinement de 400 paramètres provenant de 2052 réflexions avec $I > 2\sigma(I)$ converge à R = 0.0916 ($R_w = 0.0937$). On a aussi isolé de faibles quantités d'un produit amorphe blanc ou coquille d'oeuf qui correspond peut-être à un polymère provenant de la perte du pont phosphoré. La transposition thermique de l'adduit jaune conduit à un isomère 6,5,3 tricyclique incolore, 11, qui pourrait se former par le biais du dérivé cyclopropyle isomère 15 ou de la phosphonine à neuf chainons 7. On a confirmé la structure du composé 11 par une oxydation douce du produit de réarrangement incolore en son P-oxyde. Les cristaux de ce produit, le 2,3,6-triphényl-2-phosphatricyclo[6.1.0^{1.8}.0^{5,9}]-2-oxonona-3,6-diène-1,7,8,9-tétracarboxylate de tétraméthyle, 12, sont incolores et orthorhombiques, groupe d'espace $Pbc2_1$ (No. 29) avec a = 8,918(1), b = 22,605(4)et c = 30,169(6) Å et quatre paires de molécules par motif. L'affinement de 321 paramètres provenant de 3255 réflexions avec $I > 2\sigma(I)$ converge à R = 0.0747 ($R_w = 0.0757$). La détermination univoque des structures de ces adduits et de leurs dérivés élargit et confirme notre compréhension des réactions complexes du triphénylphosphole avec l'acétylènedicarboxylate de diméthyle.

[Traduit par la rédaction]

Introduction

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> The first reactions of 1,2,5-triphenylphosphole, 1 with dimethyl acetylenedicarboxylate gave only dimethyl 3,6-diphenylphthalate 3, a cycloaddition occurring with concomitant extrusion of the phosphorus-containing group (1). Loss of the Ph—P bridge probably occurred via a reverse Diels

Alder reaction causing loss of an appropriate fragment in the manner first proposed by Alder and Rickert, and confirmed by Cope and others (2, 3). While this reaction provided a useful component of the structure confirmation for the first synthesis of this phosphole it was not particularly valuable synthetically (4). More potentially useful was the reaction conducted under inert atmosphere and room temperature conditions, when Hughes and Uaboonkul isolated the phthalate ester **3** as obtained earlier and, in addition, two adducts that retained the phosphorus moiety (5). They assigned the spiro-biphosphole structure **4** to the yel-

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	Ester methyls	Meth	ine	Vinyl proton(s)	
Compound	δ, ppm	δ, ppm	J, Hz	δ, ppm	<i>J</i> , Hz
Yellow 2:1 adduct, 6	3.41 3.44 3.63 3.86	3.52 dd (cyclopropyl)	9.9 (P,H) 3.3 (H,H)	7.39	3.3 (H,H)
Rearranged yellow adduct, 11	2.89 3.68 3.75 3.82	4.92 d (methine)	8.4 (H,H)	6.41 dd ^b	8.4 (P,H) 8.4 (H,H)
Oxide of rearrangement product, 12	2.98 3.69 3.75 3.85	4.72 dd (methine)	1.8 (P,H) ^a 8.2	6.86 dd	8.2 (H,H) 30.8 (P,H)
Red 2:1 adduct, 8	3.16 3.25 3.62 3.71				

TABLE 1. Selected ¹H NMR spectral data for phosphole adducts in deuteriochloroform

"Uncertain assignment.

^bOverlapping. Appears as triplet. ³¹P decoupling reduces to doublet.



low 2:1 (ester to phosphole) adduct. An additional red crystalline product (mp $218-220^{\circ}C$ (dec.)) was isolated and established to be a 4:1 adduct but without structural assignment (5). They also found that the yellow spiro-biphosphole could be rearranged thermally in chloroform to a colourless isomer initially formulated as 5, and smoothly converted this to its P-oxide.



rather unusual structures assigned to the yellow 2:1 adduct and its colourless rearrangement product, and in addition to attempt to determine the structure of the red 4:1 adduct reported by the first group.



Results and discussion

Primary products

Reaction of 1,2,5-triphenylphosphole with dimethyl acetylenedicarboxylate at room temperature gave 6-10% yields of the colourless dimethyl 3,6-diphenylphthalate **3**, much lower than the 71% obtained under severe conditions (1, 2) but similar to the 9% previously obtained under mild conditions (5). This product was not examined further.

The yellow 2:1 acetylene ester: phosphole adduct was obtained in 31-35% yields, similar to that reported from the first preparation (5), and regardless of whether the reaction was conducted with neat reactants or in benzene, or whether or not freshly distilled ester or an inert atmosphere was used. Varied reaction conditions did, however, affect the yields of

Later spectroscopic and synthetic tests by Waite and Tebby led to structural reassignments of the yellow 2:1 adduct to the tricyclic, ester-stabilized, alkylidene phosphorane structure $\mathbf{6}$, and of its colourless rearrangement product to the phosphonin, a nine-membered cyclic phosphine 7 (6). These workers, who used freshly redistilled dimethyl acetylenedicarboxylate in their reactions, did not obtain any of the initially reported red adduct from their preparations.

With the current availability of higher frequency and pulsed NMR techniques not accessible to either of the previous groups, we sought to reexamine the well-reasoned though

	Quat	ernary C	Meth	nine	Ester	Ester
Compound	δ, ppm	$\overline{J, Hz}$	δ, ppm	J, Hz	δ, ppm	δ, ppm
Yellow 2:1 adduct, 6	34.8 49.5	83.0 (P,C) 3.5 (P,C)	34.5	7.8	50.5 51.4 52.3 52.6	165.7 166.0 166.6 168.4
Rearranged yellow adduct, 11	40.0 49.5 47.6 53.0	38.5 (P,C) 20.5 (P,C) 38.5 (P,C)			51.6 51.9 52.7 53.1	163.6 166.2 167.1 168.8
Oxide of rearrangement product, 12	45.5 52.3 53.9	75.1 (P,C) 3.4 (P,C) 3.3 (P,C)	51.7	13.1	52.0 52.1 52.9 53.3	163.2 165.0" 166.1 167.5
Red 2:1 adduct, 8	29.7				51.3 51.6 52.3 52.6	157.5 ^b 162.4 166.0 167.9

TABLE 2. Selected ¹³C NMR spectral data for phosphole adducts in deuteriochloroform

"Doublet. $J_{P,C} = 4.8$ Hz.

^bDoublet. $J_{P,C} = 13.1$ Hz.

TABLE 3. Coupled and decoupled ³¹P NMR spectral data for phosphole adducts

Compound	Shift, ppm (¹ H decoupled)	Coupling constants, Hz (¹ H coupled)		
Yellow 2:1 adduct, 6	34.7	d, ^a	29.9	
Rearranged yellow adduct, 11	-34.8	Quartet ^b	8.4	
Oxide of rearrangement product, 12	12.6	d triplet ^c	12.7 12.7 30.8	(P,H_1) (P,H_2) (P,H_3)
Red 2:1 adduct, 8	15.9			

"With some fine structure, several couplings in 3.3–3.6 Hz range.

^bApparent. Spacing 8.4, 8.4, 8.1 Hz; relative intensities 2.7:7.0:7.0:2.9.

^cOverlapping. Appears as quintet of relative intensities 2:4:3:4:2.

other products, as discussed later. Elemental analysis confirmed that a 2:1 adduct had been obtained, and that this sample had crystallized almost mole for mole with acetone. Melting point and spectroscopic properties of this product were essentially in agreement with those previously reported (Tables 1-3).

However, despite the detailed analysis of high-frequency proton and phosphorus NMR spectra and decoupling experiments together with various pulsed NMR techniques, it was still not possible to unequivocally assign a structure to the yellow adduct.

An X-ray structure determination on a suitable single crystal of the yellow 2:1 adduct gave confirmation that structure 6, previously assigned by Waite and Tebby (6), was the correct assignment (Tables 4–8). Figure 1 gives an ORTEP representation of the molecular structure, including the resolved hydrogen atoms. Noteworthy in this rigid framework of fused six, five, and three-membered rings is the strain imposed on the C4—P—C1 and the P—C1—C2 bonds, which are each compressed to about 12° less than the normal sp^2 bond angles. The internal angles of the cyclopropane are all very close to the expected 60°. Bonds from the

cyclopropane ring fusion to the rest of the molecule show little evidence of strain, except for an expansion of the C4—C5—C6 angle of about 12° from the normal sp^3 . Carbon-carbon bond lengths correspond quite closely to those expected for isolated single and double bonds and show negligible evidence of any electron delocalization. The shortened phosphorane carbon to phosphorus bond, the presence of which had been previously demonstrated by protonation (6), is also clearly evident from this structure determination.

The yield of red adduct varied widely with reaction conditions, unlike the yield insensitivity found for the preparation of yellow adduct **6**. About 6.5% of a red crystalline adduct was obtained from room temperature reactions using neat reagents whether the acetylene ester was used as supplied, or was redistilled just before use. Conducting the reaction in benzene caused the isolated yield to drop to 0.4%. The red product obtained here, however, melted at 198– 201°C without decomposition, rather than the 218–220°C (dec.) previously reported for a red adduct (5). It also was a 2:1 product (acetylene ester:phosphole), from NMR spectra and the X-ray crystal structure, rather than the 4:1 ad-

Parameters	Yellow adduct, 6	Red adduct, 8	Colourless P-oxide, 12
Crystal dimensions, mm	$0.27 \times 0.22 \times 0.19$	$0.13 \times 0.21 \times 0.95$	$0.08 \times 0.21 \times 0.72$
Molecular formula	C ₃₄ H ₂₉ O ₈ P	$C_{34}H_{29}O_8P$	$C_{34}H_{29}O_9P$
Method used	Elemental analysis Molecular ion from mass spectrum	Molecular ion from mass spectrum	Molecular ion from mass spectrum
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\overline{1}$ (no. 2) centrosymmetric	$P2_1/c$ (No. 14) centrosymmetric	<i>Pbc</i> 2 ₁ (No. 29) noncentrosymmetric
Unit/ cell: a b c α β γ	11.259(1) Å 12.947(3) Å 13.784(3) Å 112.25(2)° 103.44(1)° 101.80(1)°	13.233(5) Å 15.712(5) Å 17.191(7) Å 90.0° 110.35(4)° 90.0°	8.918(1) Å 22.605(4) Å 30.169(6) Å 90.0° 90.0° 90.0°
Cell volume, Å ³	1710.5	3351.2	6081.7
Z, molecules/cell	2	4	4 (pairs)
Asymmetric unit	1 molecule	1 molecule	2 molecules
Density: Calculated, g cm ⁻³ Measured, g cm ⁻³ (by flotation)	1.271 1.260	1.297 1.263	1.338 1.340
Diffractometer	Nonius + PDP11	Picker 4-circle + PDP11/10	Nonius + PDP11
Radiation	Zr-filtered Mo K_{α} $\lambda = 0.71069 \text{ Å}$	Zr-filtered Mo K_{α} $\lambda = 0.71069 \text{ Å}$	Ni-filtered Cu K_{α} $\lambda = 1.542 \text{ Å}$
Intensity measurements	$2\theta = 0.1^{\circ} - 45^{\circ}$	$2\theta = 12^{\circ} - 36^{\circ}$	$2\theta = 0^{\circ} - 130^{\circ}$
Number	2880, $I > 2\sigma(I)$	2052, $I > 2.5\sigma(I)$	3255, $I > 3\sigma(I)$
Refinement method	shelx-76, least squares ^b	SHELX-76, least squares ^b	SHELX-76, least squares ^b
Final R value Finally R _w	0.0453 0.0453	0.0916 0.0937	0.0747 0.0757
Absorption coefficient µ, cm ⁻¹	0.86	0.92	12.50

TABLE 4. Experimental crystallographic data measured at 20°C

duct reported previously. At no time was the 4:1 adduct observed, despite the testing of a variety of reaction conditions and recovery techniques.

As with the yellow 2:1 adduct, it was possible to discern many of the principal structural features of the red adduct from the high-frequency NMR data (Tables 1-3), but it was still not possible to derive an unequivocal structure entirely from this information. An X-ray crystal structure determination established that this adduct was also a phosphorane, a phosphacyclopental denylidene bonded to the α position of a stabilizing conjugated cyclopentenone, 8 (Fig. 2, and Tables 9-12). In this adduct the phosphole ring remains intact, as found previously in ylide preparations related to the testing of 1,2,5-triphenylphosphole as a phosphine for Wittig reactions (7). Carbon-carbon single bonds of the cyclopentenone involved in electron delocalization are foreshortened by about 0.1 Å as compared to the 1.53 and 1.57 Å of the single bonds not so involved (Table 6). The carbon-carbon single bonds in both the starting phosphole



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and the red adduct also are similarly foreshortened. However, there is no significant change in the lengths of the carbon-carbon single and double bonds in the phosphole ring of the adduct as compared to the starting phosphole, these being 1.38 and 1.47 Å, and 1.35 and 1.44 Å (8), respectively. All the sp^2 carbons of both five-membered rings have bond angles somewhat compressed from a normal noncyclic sp^2 carbon, the most pronounced being the compression for the P—C4—C3 angle, with a value of 106°. But

TABLE 5. Fractional atomic coordinates and temperature parameters for all non-hydrogen atoms of the yellow 2:1 adduct $6^{a,b}$

TABLE 6.	Interatomic d	listances	for all	skeletal	atoms	for	crystal
	structur	e of yelle	ow add	luct 6 (Å	a^{a}		

Atom	x/a	y/b	z/c	U_{eq}^{c}
P(1)	34422(9)	32733(8)	18764(7)	320(4)
O(1)	6092(2)	4721(2)	3500(2)	46(1)
O(2)	5981(3)	4116(2)	4809(2)	55(1)
O(3)	5361(2)	1581(2)	3676(2)	50(1)
O(4)	4269(2)	1997(2)	4869(2)	53(1)
O(5)	2696(2)	-139(2)	2842(2)	51(1)
O(6)	690(3)	-277(2)	1978(2)	61(2)
O(7)	443(2)	2181(2)	3366(2)	55(1)
0(8)	-911(2)	1502(2)	1628(2)	51(1)
C(1)	3311(3)	1975(3)	665(3)	36(2)
C(2)	2099(4)	1226(3)	246(3)	40(2)
C(3)	1151(4)	1604(3)	748(3)	39(2)
C(4)	1736(3)	2858(3)	1667(3)	33(2)
C(5)	1353(3)	1832(3)	1955(3)	34(2)
C(6)	2365(3)	1492(3)	2583(3)	32(2)
C(7)	3612(3)	2224(3)	3199(3)	33(2)
C(8)	4230(3)	3258(3)	3123(3)	33(2)
C(0)	5484(3)	4051(3)	3903(3)	38(2)
C(10)	7208(5)	5630(5)	4265(5)	72(3)
C(10)	1428(3)	1037(3)	4024(3)	37(2)
C(12)	6250(7)	1340(8)	4024(3)	91(4)
C(12)	1822(4)	200(3)	2451(3)	$\frac{1}{41}$
C(13)	1022(4)	-1313(4)	2777(6)	71(2)
C(14)	2169(0) 160(4)	1788(3)	2727(0)	40(2)
C(15)	-636(6)	2255(7)	2203(3)	40(Z) 86(A)
C(10)	-0.50(0)	4504(3)	1720(3)	33(2)
C(21)	3674(3)	5713(3)	2623(3)	$\frac{33(2)}{43(2)}$
C(22)	4230(4)	6685(4)	2023(3)	43(2)
C(23)	4394(4)	6573(4)	1359(4)	59(2)
C(24)	4190(4)	5470(4)	1339(4)	56(3)
C(25)	3614(4)	3479(4)	477(4)	30(2)
C(20)	5050(4)	4487(4)	$\frac{033(3)}{231(2)}$	47(2)
C(31)	4417(4)	1/30(3)	521(3)	37(2)
C(32)	4237(4)	793(4) 571(4)	-081(3)	47(2)
C(33)	5282(5)	371(4)	-987(4)	59(3)
C(34)	6518(5)	1298(4)	-300(4)	58(3)
C(33)	6709(4)	2238(4)	0/3(4)	53(2)
C(36)	56/9(4)	2490(4)	981(3)	44(2)
C(41)	1070(3)	3/6/(3)	1821(3)	39(2)
C(42)	248(4)	3771(4)	910(4)	54(2)
C(43)	-358(5)	4017(5)	1050(6)	81(4)
C(44)	-136(6)	5462(6)	2082(7)	93(4)
C(45)	691(7)	5484(5)	2988(6)	89(4)
C(46)	1305(4)	4635(4)	2878(4)	58(2)
O(50)	472(4)	1989(4)	6188(3)	116(3)
C(51)	1347(5)	1607(4)	6391(5)	79(3)
C(52)	1766(7)	960(6)	5457(6)	124(5)
C(53)	1909(8)	1744(9)	7527(6)	153(6)

"Estimated standard deviations are given in parentheses. Coordinates $\times 10^n$ where n = 5,4,4,4, for P,O,N,C Temperature parameters $\times 10^n$ where n = 4,3,3,3, for P,O,N,C.

^bHydrogen data have been deposited. See footnote 4

 $^{c}U_{eq}$ = the equivalent isotropic temperature parameter. $U_{eq} = 1/3 \Sigma_{j} \Sigma_{j} U_{ij} a_{i}$ * $a_{j} * (a_{i} \cdot a_{j})$. $T = \exp - (8\pi^{2} U_{iso} \sin^{2} \theta / \lambda^{2})$.

none of the angles are significantly different from the expectation for a cyclopentane or cyclopentadiene.

A further product was isolated from these reactions that contained only 4 moles of dimethyl acetylenedicarboxylate and no phosphole or fragment thereof. This product, like the red adduct isolated here, was not observed previously from these reactions. Yields of 0.7-1.8% were obtained, the lowest recoveries being achieved in those reactions which

Atoms	Distance	Atoms	Distance
C(1) - P(1)	1.815(3)	C(6)—C(5)	1.509(5)
C(4) - P(1)	1.807(4)	C(15) - C(5)	1.499(6)
C(8) - P(1)	1.750(4)	C(7) - C(6)	1.372(4)
C(21) - P(1)	1.781(4)	C(13) - C(6)	1.464(6)
C(2) - C(1)	1.343(5)	C(8) - C(7)	1.431(5)
C(31) - C(1)	1.473(6)	C(11) - C(7)	1.501(6)
C(3) - C(2)	1.469(6)	C(9) - C(8)	1.439(4)
C(4) - C(3)	1.514(4)	C(51) - O(50)	1.212(9)
C(5) - C(3)	1.527(6)	C(52) - C(51)	1.486(10)
C(5) - C(4)	1.534(6)	C(53) - C(51)	1.472(11)
C(41)—C(4)	1.495(6)		. ,

"Estimated standard deviations are given in parentheses. Mean phenyl carbon – carbon distance and standard deviation was 1.380(7) Å, range 1.352 - 1.401(5-12) Å. Mean carbon–oxygen distances and standard deviations were C=O, 1.203(5); (CO)–O, 1.343(5); and O–CH₃, 1.448(8) Å.

started with freshly redistilled acetylene ester. This suggested that the isolated product may well have been present as an impurity in the starting ester, a suspicion confirmed by literature references to this occurrence (9-12). Our detailed NMR studies of this tetramer of dimethyl acetylenedicarboxylate, a cyclopropenyl derivative of oxynorbornadiene, **9**, are in accord with the published structure. We are further examining some evidence of isomerism observed in some of the high-frequency NMR spectra of this compound.



A white, or off-white, highly insoluble material **10** was also isolated from some of these reactions. It was not possible to fully characterize this amorphous powder because of the small amounts obtained, low solubility, and its intractibility, but later we speculate briefly on the possible nature of this material.

Secondary products

The yellow 2:1 adduct **6** was rearranged by the previous group to a colourless isomer formulated as **5**, in 23% yield, by boiling a chloroform solution of the yellow adduct under reflux for 4 h (5). Repetition of this procedure confirmed that the low yield was the result of poor conversion of starting material rather than diversion of starting material to other products via side reactions. We therefore tested the use of a higher boiling solvent, 1,2-dichloroethane for this procedure. At the 22° higher temperatures much improved yields of 72–88% of the purified rearrangement product were obtained. Most improvement was obtained with short-term (5 h) reflux, or with longer refluxing times under nitrogen. The melting point and other physical properties of this rearranged material were in good agreement with the previously published data (5, 6).

Significant changes were evident in the proton NMR of the rearrangement product as compared to that of the yellow adduct 6 (Tables 1–3). Neither of the methine protons

Atoms	Angle	Atoms	Angle
C(4) - P(1) - C(1)	95.0(2)	C(15)-C(5)-C(3)	114.7(3)
C(8) - P(1) - C(1)	111.8(2)	C(15) - C(5) - C(4)	111.6(3)
C(8) - P(1) - C(4)	107.0(2)	C(15) - C(5) - C(6)	116.1(4)
C(21) - P(1) - C(1)	112.9(2)	C(7) - C(6) - C(5)	123.6(3)
C(21) - P(1) - C(4)	107.7(2)	C(13) - C(6) - C(5)	110.7(3)
C(21) - P(1) - C(8)	119.3(1)	C(13) - C(6) - C(7)	125.7(4)
C(2) - C(1) - P(1)	108.3(3)	C(8) - C(7) - C(6)	125.6(4)
C(31) - C(1) - P(1)	123.9(2)	C(11) - C(7) - C(6)	118.8(4)
C(31) - C(1) - C(2)	127.4(3)	C(11) - C(7) - C(8)	115.7(3)
C(3) - C(2) - C(1)	118.6(3)	C(7) - C(8) - P(1)	112.5(2)
C(4) - C(3) - C(2)	111.2(3)	C(9) - C(8) - P(1)	125.3(3)
C(5) - C(3) - C(2)	118.9(4)	C(9) - C(8) - C(7)	121.2(4)
C(5) - C(3) - C(4)	60.6(2)	C(22) - C(21) - P(1)	122.4(3)
C(3) - C(4) - P(1)	105.9(3)	C(26) - C(21) - P(1)	117.6(2)
C(5) - C(4) - P(1)	109.9(3)	C(32) - C(31) - C(1)	121.1(3)
C(5) - C(4) - C(3)	60.1(2)	C(36) - C(31) - C(1)	121.4(3)
C(41) - C(4) - P(1)	119.8(2)	C(42) - C(41) - C(4)	120.4(3)
C(41) - C(4) - C(3)	124.1(3)	C(46) - C(41) - C(4)	120.3(4)
C(41) - C(4) - C(5)	122.6(3)	C(52) - C(51) - O(50)	118.1(6)
C(4) - C(5) - C(3)	59.3(2)	C(53)—C(51)—O(50)	119.4(7)
C(6) - C(5) - C(3)	121.8(3)	C(53)—C(51)—C(52)	122.4(7)
C(6) - C(5) - C(4)	121.0(3)		

TABLE 7. Bond angles for all skeletal atoms of yellow adduct 6 $(deg)^a$

"Estimated standard deviations are given in parentheses. Mean phenyl carbon – carbon-carbon bond angle and standard deviation was $120.0(5)^\circ$, range $117.5^\circ-121.4(3-7)^\circ$. Range of carbon-oxygen-carbon, and carbon-carbon-oxygen bond angles was $110.7^\circ-125.2(3-4)^\circ$.

TABLE 8. Intermolecular distances of less than 3.4 Å from the crystal structure of yellow adduct 6^a

Atoms	Distance	Sym	T_x	T_y	T_{z}
$\overline{C(9)\cdots O(2)}$	3.358	-1	1	1	1
$C(22) \cdots O(4)$	3.327	-1	1	1	1
$C(23) \cdots O(4)$	3.262	-1	1	1	1
$C(3) \cdots O(6)$	3.376	-1	0	0	0
$C(10) \cdots O(7)$	3.368	-1	1	1	1
$C(34) \cdots O(8)$	3.331	1	1	0	0
$C(35) \cdots O(8)$	3.205	1	1	0	0
$C(2) \cdots O(8)$	3.238	-1	0	0	0
$C(25) \cdots O(25)$	3.487	-1	1	1	0
$C(33) \cdots O(31)$	3.521	- 1	1	0	0

"The symmetry positions are for the second atom. They are defined: 1 = x, y, z, A negative symmetry position denotes inversion. The translations (T) are applied finally.

was at high enough field to be assignable as a cyclopropyl hydrogen, and the higher field methine was now only proton coupled (and not to phosphorus). One of the methoxyls had also shifted ca. 0.5 ppm upfield. But again, despite detailed NMR studies, the structure could not be completely assigned with confidence. Even the quite reasonable assumption that there was no longer a cyclopropyl moiety in the rearranged product, from the loss of the resonance at the appropriate shift for cyclopropyl hydrogen in the ¹H NMR spectrum, would have turned out to be wrong, as will be seen shortly.

When checking the decoupled ³¹P NMR spectrum of the rearranged product **5** after it had stood for a few days in deuteriochloroform, two ³¹P resonances were noted, the new one probably that of the P oxide. A portion of the rearranged adduct was therefore oxidized and this product, the

oxide of the rearrangement product, 12, was purified and crystallized for X-ray work to ensure molecular stability of the crystal during data collection. The proton NMR spectrum of the oxide gave very similar methoxyl and methine shifts to those of the rearranged yellow adduct, except that the methine now showed a small coupling to phosphorus (Table 1). There was, however, a nearly 0.5 ppm downfield shift of the vinyl proton, explained by its proximity to the newly formed phosphoryl group, plus a sharply increased coupling of this proton to phosphorus, from 8 to 31 Hz. The same number and types of carbons were present in the two compounds from the ¹³C NMR spectra. The only changes observed were in the P-C coupling constants, which were anticipated from the change in phosphorus oxidation state. The IR spectra of the two compounds were also very similar. For these reasons it is thought that the oxidation of the rearranged adduct under mild conditions only oxidized the phosphorus of the rearrangement product 11 and did not introduce any further skeletal rearrangements.

Two enantiomers of the oxide 12 crystallized together in the unit cell, so that the X-ray structure determination required resolution of the atom locations of both enantiomers (Fig. 3, Tables 13–16). The continued presence of a cyclopropyl component in the oxide 12 was unexpected. Although this product is still a fusion of six, five, and threemembered rings, as found in the yellow adduct 6, quite complex steps are necessary to obtain the new bond locations. In the oxidized product 12 phosphorus is a component of only the six-membered ring rather than common to both the five and the six-membered rings, and the cyclopropyl no longer has any hydrogen substituents. Bond angles in the cyclopropane are all normal. Only the bond angles C3—C4—C5 and C4—C5—C6, C4—C3—C8, and C3—C8—C7 show any significant distortions caused by the



FIG. 1. ORTEP drawing of the crystal structure of the yellow 2:1 adduct 6.

SCHEME 1. Proposed pathway to the yellow 2:1 adduct 6.

SCHEME 2. Possible pathway to the colourless rearrangement product 11.

strained ring fusions. The first three are compressed $5^{\circ}-8^{\circ}$ from the normal and the last expanded to about the same extent. Bond lengths are all unremarkable.

Reaction and rearrangement pathways

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The likely steps involved in the formation of the yellow 2:1 adduct **6** of dimethyl acetylenedicarboxylate to the phosphole **2** can be plausibly outlined as shown in Scheme 1. Provision of polar versus nonpolar conditions (neat reagents versus reaction in benzene) made a negligible difference to the yield, suggesting that none of the rates of the

individual steps of initial formation of the zwitterion 13, ring closure to structure 14 nor the following electrocyclic rearrangement to the product 6, are overwhelmingly rate-determining. Our experimental observations are completely in accord with this reaction path, which is very similar to that previously proposed for this reaction by Waite and Tebby (6).

Scheme 2 gives a suggested pathway for rearrangement of adduct 6 to the colourless isomer 11. It involves intermediate formation of a cyclopropane, which is retained in the final product. The carbocation formed is secondary and

allylically stabilized and the anionic center required is stabilized via the adjacent carbonyl.

While it is possible to involve the *cis, cis, trans, cis* phosphonin 7 proposed by Waite and Tebby (6) in the pathway to the observed product **11**, this would require an additional step to reach structure **15**. Support is given to this possibility, however, from atom and electronic proximities noted from molecular models of this geometry as well as from the facile formation of the dihydrophosphindole oxide **17** from the *cis, cis, cis, trans* phosphonin oxide **16** (13). The presence of two benzo groups in the phosphonin prevents formation of the phosphindole (14).

A possible pathway to the red 2:1 adduct 8 from the

related compound 21 prepared from tri-p-tolylphosphine and the acetylene ester, which is also analogous to the red adduct 8 (17).

An equally plausible outcome from intermediate 18 on paper could have been the phosphole 22, from direct closure of the zwitterion. As far as we are aware, however, compound 22 has not been isolated from any reaction of the acetylene ester with triphenylphosphine. It has at least been implicated in this reaction by the observed formation of another stable product, compound 23, via migration of a phenyl group of intermediate 22 (18).

Compound 4, analogous to 22, was proposed as the structure of an adduct from the reaction of 1,2,5-triphenyl-phosphole with the acetylene ester. But we now know that it is not likely that spiro-biphosphole 4 forms from this interaction, even as an intermediate, since it would be diffi-

cult to sketch a plausible pathway from the spiro product to any of the adducts yet isolated from this reaction.

It should be mentioned here by way of a further precedent for the structure assigned to the red adduct that structure **25** has been proposed for a yellow 2:1 adduct of dimethyl acetylenedicarboxylate with the phosphindole **24**

TABLE 9. Fractional atomic coordinates and temperature parameters of all non-hydrogen atoms of red 2:1 adduct $\mathbf{8}^a$

TABLE 10.	Interatomic distances for all skeletal atoms from the	
	crystal structure of the red adduct 8 (Å)"	

Atom	x/a	y/b	z/c	$U_{ m eq}$
P(1)	73782(23)	19558(17)	7314(17)	442(12)
C(1)	8667(9)	1424(7)	1238(7)	54(5)
C(2)	8679(10)	1215(7)	2016(7)	63(6)
C(3)	7705(10)	1450(7)	2229(7)	64(6)
C(4)	6901(9)	1866(7)	1615(6)	51(5)
C(21)	6504(8)	1294(7)	-82(7)	52(5)
C(22)	5618(9)	1674(8)	-726(7)	64(5)
C(23)	4879(10)	1143(8)	-1296(8)	76(6)
C(24)	5023(11)	272(10)	-1231(8)	76(7)
C(25)	5907(11)	-107(8)	-614(8)	70(6)
C(26)	6657(10)	414(7)	-30(7)	62(6)
C(31)	5854(9)	2142(7)	1603(7)	50(5)
C(32)	5236(10)	2721(7)	983(8)	68(6)
C(33)	4214(11)	2977(9)	975(9)	85(7)
C(34)	3800(12)	2652(10)	1547(11)	96(8)
C(35)	4427(13)	2066(11)	2157(9)	93(8)
C(36)	5454(10)	1804(7)	2172(7)	61(6)
C(41)	9491(9)	1321(7)	865(8)	59(6)
C(42)	9222(10)	1472(7)	18(7)	57(5)
C(43)	10060(11)	1378(8)	-336(8)	75(6)
C(44)	11087(12)	1139(9)	159(9)	86(8)
C(45)	11333(10)	989(8)	1008(9)	79(7)
C(46)	10542(10)	1078(8)	1386(8)	73(6)
C(5)	7504(8)	2998(6)	438(5)	41(4)
C(6)	7799(8)	3716(7)	961(6)	41(4)
C(7)	7871(8)	4442(7)	544(7)	51(5)
C(8)	7615(9)	4247(7)	-361(6)	46(5)
C(9)	7419(8)	3252(7)	-383(7)	45(5)
C(10)	9388(10)	4022(9)	-353(9)	88(7)
C(11)	6583(11)	4623(7)	-925(7)	52(6)
C(12)	4652(11)	4786(10)	-1159(10)	117(8)
C(13)	8139(10)	5268(8)	921(8)	62(6)
C(14)	8279(13)	6767(7)	714(10)	110(9)
C(15)	8026(10)	3681(7)	1862(7)	47(5)
C(16)	7260(11)	3921(8)	2935(7)	84(7)
O(1)	7264(6)	2840(4)	-1026(4)	56(3)
O(2)	8387(7)	4469(5)	-708(5)	66(4)
O(3)	5774(7)	4479(5)	-641(5)	81(4)
O(4)	6441(7)	4997(6)	-1545(6)	92(5)
O(5)	7985(7)	5907(5)	375(5)	75(4)
O(6)	8506(-8)	5397(-5)	1659(-6)	94(5)
O(7)	7187(-7)	3978(-5)	2059(-4)	65(4)
O(8)	8821(-7)	3398(5)	2354(5)	75(4)
C(51)	1244(20)	3765(17)	2010(16)	211(10)'
C(52)	1330(27)	3412(19)	2919(22)	313(16)'
U(53)	2082(23)	4336(17)		

"Estimated standard deviations are given in parentheses. Coordinates $\times 10^{n}$ where n = 5,4,4,4, for P,O,N,C. Temperature parameters $\times 10^{n}$ where n = 4,3,3,3, for P,O,N,C.

 ${}^{b}U_{eq}$ = the equivalent isotropic temperature parameter. $U_{eq} = 1/3 \sum_{j} \sum_{j} U_{ij} a_{j}$ * $a_{j} * (a_{i} \cdot a_{j})$. Primed values indicate that U_{iso} is given. $T = \exp - (8\pi^{2}U_{iso} \sin^{2} \theta/\lambda^{2})$.

(19). It was suggested that the observed loss of the atom of oxygen in the formation of **25** occurred via an intermediate oxirane rearrangement product.

Finally, a brief speculation on the nature of the white or buff, highly insoluble, amorphous powder that was also isolated from some of the phosphole – acetylene ester reactions. This is quite possibly poly(phenylphosphinidene), $(C_6H_5P)_n$, or an oxidized version of this, $(C_6H_5P)_n(C_6H_5PO)_m$, formed from the 1:1 acetylene adduct that lost the phospho-

Atoms	Distance	Atoms	Distance
C(1) - P(1)	1.826(11)	C(9)—C(5)	1.434(16)
C(4) - P(1)	1.843(13)	C(7) - C(6)	1.368(16)
C(21) - P(1)	1.802(10)	C(15) - C(6)	1.472(15)
C(5) - P(1)	1.738(10)	C(8) - C(7)	1.503(16)
C(2) - C(1)	1.371(18)	C(13) - C(7)	1.440(17)
C(41) - C(1)	1.454(20)	C(9) - C(8)	1.582(15)
C(3) - C(2)	1.504(20)	C(11) - C(8)	1.495(15)
C(4) - C(3)	1.375(14)	O(2) - C(8)	1.395(16)
C(31) - C(4)	1.445(18)	O(1) - C(9)	1.236(14)
C(6)C(5)	1.411(14)		

"Estimated standard deviations are given in parentheses. Mean phenyl carbon – carbon distance and standard deviation was 1.405(19) Å, range 1.370-1.446(14-23) Å. Mean carbon–oxygen distances and standard deviations were C=O, 1.188(15); (CO)–O, 1.345(17); and O–CH₃, 1.488(15) Å.

FIG. 2. ORTEP drawing of the crystal structure of the red 2:1 adduct $\mathbf{8}$.

rus bridge to yield dimethyl 3,6-diphenylphthalate. Or it could be a copolymer of the phosphorus fragment with some incorporation of acetylene ester $(C_6H_5P)_n(CH_3O_2C-C==C-CO_2CH_3)_m$, since the NMR shows the presence of ester methyl. In the absence of sufficient material for full characterization of this product these possibilities could not be better established. However, support for these suggestions is obtained from the reported isolation of poly(phenylphosphinidene oxide) from an analogous reaction of pentaphenylphosphole oxide with benzyne (20).

Experimental

Infrared spectra were obtained on KBr pellets scanned on a Perkin Elmer model 1330 instrument calibrated with polystyrene film.

Atoms	Angle	Atoms	Angle			
$\begin{array}{c} \hline C(4) & -P(1) - C(1) \\ C(21) & -P(1) - C(1) \\ C(21) - P(1) - C(4) \\ C(5) - P(1) - C(4) \\ C(5) - P(1) - C(4) \\ C(5) - P(1) - C(21) \\ C(2) - C(1) - P(1) \end{array}$	95.9(5) 110.3(5) 106.4(5) 113.7(5) 114.0(5) 114.8(5) 105.5(9)	$\begin{array}{c} C(26) - C(21) - P(1) \\ C(6) - C(5) - P(1) \\ C(9) - C(5) - P(1) \\ C(9) - C(5) - C(6) \\ C(7) - C(6) - C(5) \\ C(15) - C(6) - C(5) \\ C(15) - C(6) - C(7) \end{array}$	118.8(7) 127.0(8) 124.5(8) 108.3(9) 112.7(9) 123.4(10) 123.8(10)			
C(41) - C(1) - P(1) $C(41) - C(1) - C(2)$ $C(3) - C(2) - C(1)$ $C(4) - C(3) - C(2)$ $C(3) - C(4) - P(1)$ $C(31) - C(4) - P(1)$ $C(31) - C(4) - C(3)$ $C(22) - C(21) - P(1)$	$124.0(9) \\130.4(10) \\117.3(10) \\115.4(11) \\105.9(10) \\124.5(8) \\129.5(12) \\119.4(9)$	C(8)C(7)C(6)C(13)C(7)C(6)C(13)C(7)C(8)C(9)C(8)C(7)C(11)C(8)C(7)C(11)C(8)C(9)C(8)C(9)C(5)	109.9(9) 124.5(11) 125.5(11) 101.7(9) 114.6(10) 105.6(8) 107.2(9)			

TABLE 11. Bond angles for all skeletal atoms of the red adduct 8 $(deg)^a$

"Estimated standard deviations are given in parentheses. Mean phenyl carbon – carbon– carbon bond angle and standard deviation was 120.0(12)°, range 117.1°-122.9(9-16)°. Range of carbon–oxygen–carbon and carbon–carbon–oxygen bond angles was 105.3°-124.9(8-14)°.

SCHEME 3. Pathway to the red 2:1 adduct 8 from 1,2,5-triphenylphosphole and dimethyl acetylenedicarboxylate.

TABLE 12. Intermolecular distances of less than 3.4 Å from the crystal structure of the red adduct 8 $(Å)^a$

Atoms	Distance	Sym	T_x	T_y	T_z
$O(53) \cdots C(2)$	3.399	2	1	0	0
$O(53) \cdots C(3)$	3.383	2	1	0	0
$O(1) \cdots C(36)$	3.238	-2	0	1	0
$O(6) \cdots C(46)$	3.329	2	2	0	0
$O(7) \cdots C(12)$	3.078	-1	1	1	0
$O(1) \cdots C(16)$	3.292	-2	0	1	0
$O(53) \cdots O(2)$	3.300	-1	1	1	0
$O(53) \cdots O(4)$	2.983	-1	1	1	0
$O(52) \cdots O(8)$	3.118	1	-1	0	0

"The symmetry positions are for the second atom. They are defined: $2 = -x, \frac{1}{2} + y, \frac{1}{2} - z$, A negative symmetry position denotes inversion. The translations (*T*) are applied finally.

Where useful, absorptions have been noted thus: s = strong, m = medium, w = weak, b = broad. UV spectra were obtained on a Philips PU 8740 UV/VIS spectrophotometer. Routine NMR spectra were recorded on a Perkin Elmer R-12 60 MHz instrument using solutions in deuteriochloroform at room temperature, unless otherwise specified. More detailed NMR experiments were performed on a Bruker WM 250 instrument, or, particularly for optimum resolution of coupled ³¹P spectra, at 145.78 MHz on a Bruker AMX 360 spectrometer. Decoupling, nuclear Overhauser effect, or DEPT experiments were conducted wherever necessary to aid in assignments. Melting points were conducted on a Reichert type 7905 hot stage microscope or on a Gallenkamp model MF-370 Kofler aluminum block apparatus and are uncorrected. Mass spectra

were determined on a Finnigan 3300 GC/MS system. Elemental analysis was by Canadian Microanalytical Service Ltd., Vancouver.

Reaction of 1,2,5-triphenylphosphole with neat dimethyl acetylenedicarboxylate

The finely ground phosphole (2.04 g; 6.52 mmol) was placed in a 100 mL round bottom flask fitted with a septum and flushed with oxygen-free nitrogen for 10 min. Dimethyl acetylenedicarboxylate (as supplied, Aldrich), 20 mL (163 mmol), was added via a syringe, with stirring. The initially yellow solution became red during 1 h, and then gradually turned dark brown.

After stirring the reaction mixture for 2 days at room temperature under nitrogen, it was filtered to recover 207 mg of white crystals, mp 183-186°C, identified as dimethyl 3,6-diphenylphthalate 3 by melting point and 'H NMR (60 MHz), 7.5-7.0 ppm (multiplet, 12H), 3.6 (singlet, 6H). Filtration of the mother liquor after standing a further 2 days, no longer under nitrogen, gave a further 1.43 g of orange crystals. A portion of this recrystallized from ethanol, ethanol-chloroform, and then 100% ethanol gave 0.56 g of yellow crystals, mp 159-161°C without decomposition. This was identified from the X-ray structure determination as tetramethyl 1,6,7-triphenyI-6-phospha(V)tricyclo[7.3.1.0^{1,9}]nona-3,5,7-triene-2,3,4,5-tetracarboxylate, the yellow adduct 6. ¹H NMR (250 MHz) ppm: aromatic plus one vinyl proton 6.6-7.5 (16H), ester methyl resonances at 3.41 (3H), 3.44 (3H), 3.63 (3H), 3.86 (3H), and one methine resonance as a doublet of doublets centered at 3.52 ppm. ¹³C NMR (250 MHz) ppm: carbonyl carbons 168.4, 166.6, 166.0, 165.7; ester methyl carbons, 52.6, 52.3, 51.4, 50.5; methine carbon doublet centered at 34.5, J_{PC} 7.8 Hz; quaternary carbons, doublet centered at 34.8, J_{PC} 83.0 Hz; 49.5, J_{PC} 3.5 Hz; peak positions (relative intensities) for aromatic and olefinic carbons, some overlap and some coupled to phosphorus 146.1

TABLE 13. Fractional atomic coordinates and temperature parameters for the two enantiomers of the oxide of the rearrangement product 12^a

TABLE 13 (concluded)							
Atom	x/a	y/b	z/c	$U_{\rm eq}^{\ \ b}$			
C(107)	3885(10)	-2113(4)	-2175(3)	30(2)			
C(108)	3090(12)	-1578(4)	-1972(3)	35(2)			
C(109)	5248(13)	-891(5)	-2946(4)	44(2)			
C(110)	7621(15)	-1077(7)	-3270(5)	79(3)			
Č(111)	5948(12)	-1281(4)	-1995(4)	38(2)			
C(112)	7972(14)	-1537(6)	-1518(4)	60(3)			
C(113)	4660(12)	-2536(5)	-1875(3)	39(2)			
C(114)	6599(16)	-3231(6)	-1824(5)	76(3)			
C(115)	2990(13)	-1508(4)	-1475(4)	40(2)			
C(116)	1345(15)	-1597(6)	-870(4)	61(3)			
C(121)	2804(11)	-3223(4)	-2507(3)	35(2)'			
C(122)	3717(13)	-3650(5)	-2710(4)	51(3)'			
C(123)	3439(15)	-4263(6)	-2600(5)	62(3)'			
C(124)	2357(14)	-4406(6)	-2305(4)	58(3)'			
C(125)	1472(15)	-3985(6)	-2087(4)	65(3)'			
C(126)	1722(13)	-3388(5)	-2191(4)	51(3)'			
C(131)	150(11)	-2545(5)	-2985(3)	36(2)'			
C(132)	742(12)	-2807(5)	-3365(4)	44(2)'			
C(133)	-282(16)	-3125(6)	-3655(5)	74(3)'			
C(134)	-1830(18)	-3119(7)	-3569(6)	90(4)'			
C(135)	-2373(16)	-2839(7)	-3207(5)	80(3)'			
C(136)	-1407(14)	-2561(5)	-2886(4)	53(3)'			
C(141)	1793(12)	-607(4)	-2940(3)	37(2)'			
C(142)	1091(13)	-93(5)	-2794(4)	52(3)'			
C(143)	347(15)	269(6)	-3113(5)	70(3)'			
C(144)	216(15)	89(6)	-3548(5)	68(3)'			
C(145)	806(16)	-442(6)	-3681(5)	73(3)'			
C(146)	1667(13)	-784(5)	-3377(4)	47(3)'			
H(101)	-39(5)	-160(4)	-252(3)	6(1)'			
H(102)	135(5)	-103(3)	-209(3)	4(1)'			

"Estimated standard deviations are given in parentheses. Coordinates \times 10" where n = 5,4,4,4, for P,O,N,C Temperature parameters \times 10' where n = 4,3,3,3, for P,O,N,C.

 ${}^{b}U_{cq}$ = the equivalent isotropic temperature parameter. $U_{cq} = 1/3 \sum_{i} \sum_{j} U_{ij} a_{i}$ * a_j * $(a_i \cdot a_j)$. Primed values indicate that U_{iso} is given. $T = \exp - (8\pi^2 U_{iso})$ $\sin^2 \theta / \lambda^2$).

(3.8), 145.7 (3.7), 133.0 (12.6), 132.8 (9.2), 131.8 (2.7), 131.4 (1.9), 131.2 (2.2), 131.0 (1.5), 130.1 (5.8), 129.5 (6.9), 129.12 (17.5), 129.05 (10.2), 128.6 (7.4), 128.2 (13.4), 128.0 (14.7), 126.9 (9.6), 126.8 (7.4), 120.0 (1.3), 118.5 (1.2). A combined total of 1.203 g of 6 was recrystallized twice more from acetone and dried in vacuo for an analytical sample. Anal. (adduct cocrystallized with 0.74-mol of acetone, determined by integrated 60 MHz ¹H NMR) calcd. for $C_{34}H_{29}PO_8 \cdot 0.74 C_3H_6O$: C 68.02, H 5.27, P 4.84%; found: C 67.87, H 5.16, P 3.77%. Mass spectrum, methane CI, 200°C probe temp. (relative intensity), calcd. for C₃₄H₂₉O₈P: 596; found: M + 1, 597(100); M + 29, 625(15); M + 41, 637(6).

Further recrystallizations of the yellow adduct 6 from acetone and 95% ethanol produced X-ray quality crystals, mp 167-169°C. UV (95% EtOH) λ_{max} nm (log ϵ): 202 (4.77), 225 (4.47), 269 (4.27), 349 (4.00), 392 (3.78). IR (KBr) cm⁻¹: 3060w, 2950w, 1735s, 1700w, 1680m, 1650s, 1635m, 1500m, 1430m, 1340m, 1310m, 1280m, 1235s, 1210s, 1140m, 1110m, 1065w, 760m, 700m, 695m.

The residual mother liquors were combined and chromatographed on 40-140 mesh silica gel (Bakersil, 128 g) in a 4 cm diameter column. Rechromatography of combined similar fractions (from TLC tests) on Davisil 62 silica gel (60-200 mesh) enabled a further 99 mg of yellow crystals of 3 and a total of 255 mg of red crystals of impure adduct 8 to be recovered. Recrystallization of the red adduct twice more from acetone gave pure material, mp 198-201°C.

Atom	x/a	y/b	z/c	U_{eq}^{b}
 P(1)	19170(1)	10300(1)	0(1)	331(8)
P(101)	30634(30)	-24677(11)	-26720(9)	306(7)
$\dot{O(1)}$	1116(8)	932(3)	413(2)	45(2)
O(2)	-291(9)	-939(3)	482(3)	52(2)
O(3)	-1599(9)	-138(3)	263(3)	51(2)
O(4)	-1461(9)	-595(3)	-680(3)	53(2)
O(5)	-1702(9)	325(3)	-899(2)	48(2)
O(6)	842(8)	1196(4)	-1187(2)	47(2)
O(7)	-649(9)	1433(3)	-608(3)	48(2)
O(8)	1093(9)	-136(3)	-1419(3)	53(2)
O(9)	3350(8)	260(3)	-1324(2)	40(2)
C(1)	3892(11)	756(5)	0(3)	37(2)
C(2)	4244(13)	258(4)	-208(3)	40(2)
C(3)	3120(12)	-146(4)	-414(3)	34(2)
C(4)	2236(11)	-436(4)	-39(3)	33(2)
C(5)	756(10)	-288(4)	-52(3)	27(2)
C(6)	391(11)	74(4)	-455(3)	30(2)
C(7)	1138(11)	684(4)	-490(3)	33(2)
C(8)	1914(12)	145(4)	-690(3)	32(2)
C(9)	-403(12)	-500(5)	256(3)	39(2)
C(10)	-2870(13)	-325(6)	547(4)	57(3)
C(11)	-1011(12)	-110(5)	-691(3)	38(2)
C(12)	-3080(15)	164(6)	-1143(5)	65(3)
C(13)	446(12)	1126(4)	-817(3)	31(2)
C(14)	-1459(16)	1875(6)	-891(5)	76(3)
C(15)	2056(12)	85(4)	-1186(3)	34(2)
C(16)	3656(14)	173(5)	-1794(4)	53(2)
C(21)	2192(12)	1826(5)	-137(4)	43(2)
C(22)	3134(13)	1983(5)	-4/2(4)	46(2)
C(23)	3364(14)	2601(6)	-56/(4)	58(3)
C(24)	2567(15)	3002(6)	-304(5)	/1(3)'
C(25)	1669(15)	2835(6)	33(S) 121(4)	69(3)
C(26)	1460(13)	2230(5)	131(4)	49(3)
C(31)	5003(11)	1123(4)	256(3)	$29(2)^{\circ}$
C(32)	0430(14)	1104(5)	91(4)	54(5) 60(2)/
C(33)	7349(14)	1316(0)	343(4)	52(3)'
C(34)	5638(14)	1793(3) 1740(5)	740(4)	52(5) 51(2)'
C(35)	3038(14) 4570(12)	1/40(3)	630(4)	$\frac{31(3)}{41(2)'}$
C(30)	4379(12) 2075(12)	-755(4)	320(3)	$\frac{41(2)}{34(2)'}$
C(41)	2651(14)	-1322(6)	232(3)	57(3)'
C(42)	4300(16)	-1643(6)	574(5)	68(3)'
C(43)	4257(16)	-1427(6)	994(5)	71(3)'
C(45)	3741(16)	-862(7)	1092(5)	77(3)'
C(46)	3069(14)	-504(5)	748(4)	52(3)'
H(1)	530(5)	7(3)	-21(3)	5(1)'
H(2)	371(5)	-36(3)	-63(3)	5(1)'
O(101)	3992(8)	-2400(3)	-3070(2)	43(2)
O(102)	5128(10)	-453(4)	-3161(3)	69(2)
O(103)	6435(9)	-1251(4)	-2962(3)	58(2)
O(104)	6387(10)	-768(3)	-2011(3)	58(2)
O(105)	6684(8)	-1715(4)	-1780(3)	54(2)
O(106)	4317(9)	-2621(3)	-1495(3)	55(2)
O(107)	5733(8)	-2812(3)	-2085(2)	46(2)
O(108)	3908(8)	-1276(4)	-1244(3)	55(2)
O(109)	1642(8)	-1696(3)	-1333(2)	44(2)
C(101)	1174(11)	-2199(4)	-2699(3)	34(2)
C(102)	766(11)	-1698(4)	-2486(3)	31(2)
C(103)	1848(11)	-1288(4)	-2250(3)	34(2)
C(104)	2675(12)	-961(5)	-2613(3)	40(2)
C(105)	4122(12)	-1102(4)	-2615(3)	38(2)
C(106)	4578(12)	-1481(4)	-2221(3)	34(2)

TABLE 14. Interatomic distances for all skeletal atoms of the two enantiomers of the oxide of the rearrangement product $12 (\text{\AA})^a$

$\begin{array}{c c c c c c c c c c c c c c c c c c c $				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Atoms	Distance	Atoms	Distance
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(1) - P(1)	1.454(7)	C(11)-C(6)	1.497(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(1) - P(1)	1.867(10)	C(8)C(7)	1.526(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(7) - P(1)	1.810(9)	C(13) - C(7)	1.534(13)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(21) - P(1)	1.862(11)	C(15)C(8)	1.509(13)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(101) - P(101)	1.467(7)	C(102) - C(101)	1.352(13)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(101) - P(101)	1.793(10)	C(131) - C(101)	1.480(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(107) - P(101)	1.850(10)	C(103) - C(102)	1.517(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(121) - P(101)	1.794(10)	C(104) - C(103)	1.514(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(2) - C(1)	1.328(14)	C(108) - C(103)	1.535(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(31) - C(1)	1.505(14)	C(105) - C(104)	1.330(15)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(3) - C(2)	1.489(15)	C(141) - C(104)	1.493(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(4) - C(3)	1.527(14)	C(106) - C(105)	1.519(14)
$\begin{array}{ccccccc} C(5) - C(4) & 1.363(13) & C(107) - C(106) & 1.563(13) \\ C(41) - C(4) & 1.479(14) & C(108) - C(106) & 1.541(15) \\ C(6) - C(5) & 1.502(13) & C(111) - C(106) & 1.470(14) \\ C(9) - C(5) & 1.469(14) & C(108) - C(107) & 1.530(13) \\ C(7) - C(6) & 1.535(13) & C(113) - C(107) & 1.489(14) \\ C(8) - C(6) & 1.541(14) & C(115) - C(108) & 1.510(14) \\ \end{array}$	C(8) - C(3)	1.511(14)	C(109) - C(105)	1.496(15)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(5) - C(4)	1.363(13)	C(107) - C(106)	1.563(13)
$\begin{array}{ccccccc} C(6) & -C(5) & 1.502(13) & C(111) - C(106) & 1.470(14) \\ C(9) - C(5) & 1.469(14) & C(108) - C(107) & 1.530(13) \\ C(7) - C(6) & 1.535(13) & C(113) - C(107) & 1.489(14) \\ C(8) - C(6) & 1.541(14) & C(115) - C(108) & 1.510(14) \\ \end{array}$	C(41) - C(4)	1.479(14)	C(108) - C(106)	1.541(15)
$\begin{array}{cccc} C(9) - C(5) & 1.469(14) & C(108) - C(107) & 1.530(13) \\ C(7) - C(6) & 1.535(13) & C(113) - C(107) & 1.489(14) \\ C(8) - C(6) & 1.541(14) & C(115) - C(108) & 1.510(14) \end{array}$	C(6) - C(5)	1.502(13)	C(111) - C(106)	1.470(14)
$\begin{array}{cccc} C(7) & -C(6) & 1.535(13) & C(113) - C(107) & 1.489(14) \\ C(8) - C(6) & 1.541(14) & C(115) - C(108) & 1.510(14) \\ \end{array}$	C(9) - C(5)	1.469(14)	C(108) - C(107)	1.530(13)
C(8) - C(6) 1.541(14) $C(115) - C(108)$ 1.510(14)	C(7) - C(6)	1.535(13)	C(113)-C(107)	1.489(14)
	C(8)—C(6)	1.541(14)	C(115)—C(108)	1.510(14)

"Estimated standard deviations are given in parentheses. Mean phenyl carbon – carbon distance and standard deviation was 1.402(18) Å, range 1.351-1.461(15-23) Å. Mean carbon–oxygen distances and standard deviations were C=O, 1.199(13); (CO)–O, 1.330(13); and O–CH₃, 1.466(15) Å.

Recrystallization of pure red compound 8 from 95% ethanol gave X-ray quality crystals, mp 198-199°C without decomposition. UV (95% EtOH) λ_{max} nm (log ϵ): 203 (4.74), 224 (4.37), 273 (4.09), 384 (4.27). IR (KBr) cm⁻¹: 3060w, 2950w, 1750s, 1690m, 1645m, 1545m, 1495w, 1435w, 1350m, 1330m, 1235s, 1210s, 1180s, 1160m, 1115m, 1055w, 760m, 750m, 690m, 580w. ¹H NMR (250 MHz) ppm: aromatic 7.9-7.09 (17H), methoxyl hydrogen resonances at 3.71 (3H), 3.62 (3H), 3.25 (3H), 3.16 (3H). ¹³C NMR (250 MHz) ppm: carbonyl carbons 167.9, 166.0, 162.4, 157.6, ester methyl carbons 52.6, 52.3, 51.6, 51.3; quaternary carbon 29.7; peak positions (relative intensities) for aromatic and olefinic carbons, some overlap and some coupled to phosphorus 137.1 (3.2), 136.8 (3.6), 136.7 (3.6), 136.4 (3.3), 136.3 (1.4), 134.9 (1.1), 134.7 (1.4), 134.0 (4.4), 133.4 (2.2), 133.3 (6.4), 133.1 (6.0), 131.3 (1.7), 131.23 (1.9), 131.16 (1.6), 129.9 (7.9), 129.8 (8.0), 129.5 (7.2), 129.3 (9.0), 129.1 (17.7), 128.3 (0.8), 127.4 (6.6), 127.3 (7.6), 127 (7.2), 126.9 (6.4), 117.4 (1.3), 116.0 (1.2), 114.2 (0.6), 109.9 (0.7), 109.7 (0.7). Mass spectrum, methane CI, 350°C probe temp., calcd. for C₃₄H₂₉O₈P: 596; found: M + 1, 597. Recrystallization several times from toluene gave what appeared to be a different polymorph of the same compound, mp 251-252°C, and an identical 250 MHz 'H NMR, identified to be trimethyl 1,2,5-triphenylphosphoranylidene-4-methoxycyclopent-2-ene-5-one-2,3,4-tricarboxylate, 8, from the X-ray determination.

An off-white powder identified as **10** (11.8 mg; mp 185°C) was also isolated. UV (95% EtOH) λ_{max} nm: 202, 219, 257, 368; molecular weight and hence extinction coefficients not known. IR (KBr) cm⁻¹: 3060, 3010, 2960, 1740, 1590, 1500, 1460, 1435, 1360, 1290, 1250, 1200, 1180, 1110, 1000, 1055, 910, 700, 520. ¹H NMR (250 MHz), high intensity peak positions, ppm (intensity): 7.26 (19), 7.10 (1.7), 4.90 (1.2), 4.12 (1.4), 4.06 (1.6), 3.98 (10.4, 3H), 3.96 (10.4, 3H), 3.82 (10.3, 3H), 3.65 (10.1, 3H), 3.59 (10.6, 3H), 3.39 (10.2, 3H), 3.28 (1.2), 3.21 (1.1), 2.16 (1.3). ³¹P NMR (250 MHz): +55.77 ppm.

From the column fractions a total of 0.41 g of an acetylene tetramer was also isolated, identified as tetramethyl 4-meth-

oxy-5[1,2,3-tris (methoxycarbonyl)-2-cyclopropen-1-yl]-7-oxabicyclo[2,2,1]hepta-2,5-diene-1,2,3,6-tetracarboxylate **9**, via comparison of the physical properties with published values (refs. 9– 12). IR (KBr) cm⁻¹: 3000w, 2960m, 2850w, 1875m, 1755s, 1735s, 1720s, 1620m, 1435s, 1350s, 1335s, 1295s, 1275s, 1205s, 1140s, 1060s, 1003m, 980m, 965m, 905w, 770w, 720w. ¹H NMR (60 MHz) ppm: 3.89 (12H), 3.78 (3H), 3.75 (3H), 3.67 (3H), 3.61 (3H); in acetone- d_6 (60 MHz): 3.86 (3H), 3.78 (6H), 3.76 (3H), 3.7 (3H), 3.66 (3H), 3.6 (3H), 3.54 (3H). ¹H NMR in CDCl₃ (250 MHz) each integrating for 3H: 3.87, 3.85, 3.84, 3.83, 3.74, 3.70, 3.63, and 3.56 ppm.

Reaction of 1,2,5-triphenylphosphole with dimethyl acetylenedicarboxylate in benzene

A solution of 2.3 g (6.52 mmol) of the finely ground phosphole was made up under oxygen-free nitrogen in 50 mL of benzene dried over Molecular Sieve 4A by gentle warming in a water bath. After cooling the solution to room temperature, dimethyl acetylenedicarboxylate (Aldrich), 20 mL (163 mmol), was added to the solution all at once via a syringe. The initially yellow solution changed to deep red within minutes and then turned dark brown.

After stirring the solution for 2 days at room temperature, the reaction mixture was filtered to give 1.10 g of yellow solid, mp $163-165^{\circ}$ C, which was identified as the previously isolated yellow adduct **6**. Further impure **6** (0.395 g) was obtained in a second crop, which when recrystallized yielded a further 0.26 g of pure material, mp $159-163^{\circ}$ C.

The volume of the mother liquor was reduced and the solution was allowed to crystallize further to yield white needles (0.29 g), mp 186–189°C, ¹H NMR (60 MHz) ppm: 7.5–7.0 (12H), 3.6 (6H). This was identified as dimethyl 3,6-diphenylphthalate **3** from the NMR spectrum.

The collected mother liquors were reduced in volume and the residue was taken up in a minimum volume of chloroform, chromatographed on silica gel (Merck 70–230 mesh, 120 g) in a 2.5 cm diameter column, and eluted with chloroform. Selected fractions were crystallized from acetone to yield a further 0.15 g of impure yellow adduct **6** and 18 mg of the red adduct **8**. A quantity of the acetylene tetramer **9** (0.313 g) was also isolated, mp 89–91°C, and ¹H NMR was identical to that of the previously isolated material.

A small amount of off-white powder **10** (110 mg) was also obtained. UV (95%EtOH) λ_{max} nm: 202, 219, 257, 368, again molecular weight unknown. IR (KBr) cm⁻¹: 3060w, 3010m, 2960w, 1740s, 1710s, 1590s, 1500s, 1460s, 1435s, 1360m, 1290s, 1250s, 1200s, 1180s, 1110m, 1065m, 1055w, 1010m, 910m, 700m, 695m, 520m. ¹H and ³¹P NMR spectra were identical to those of **10** isolated from the 1,2,5-triphenylphosphole reaction with neat DMADC. This was not further characterized.

The last fraction of the previous column was reduced in volume and chromatographed on silica gel (Merck 70–230 mesh, 160 g) in a 2.5 cm diameter column. Crystallization of combined similar fractions from CCl₄ enabled recovery of 0.299 g of a tan powder, UV (95% EtOH) λ_{max} nm: 200, 219, 261 (molecular weight unknown). IR (KBr) cm⁻¹: 3400br, 3055w, 2950w, 1725m, 1650br, 1440w, 1385m, 1220 broad, 1140m, 1065m, 1050w, 750w, 700w, 560w, which also could not be identified.

Reaction of phosphole 2 with neat freshly distilled acetylene ester

The acetylene ester (20 mL) was distilled under reduced pressure (2 Torr; 1 Torr = 133.3 Pa) in an inert atmosphere to recover a sharp cut of 15 mL of the pure material. The residual viscous oil from the distillation was dissolved in 95% ethanol and allowed to crystallize to yield 2.13 g of clear crystals, identified by IR as the tetramer of the acetylene ester, **9**.

The distilled acetylene ester (15 mL, 122 mmol) was added all at once via syringe to 4.01 g (1.28 mmol) of finely ground 1,2,5triphenylphosphole, in a flask that had been previously flushed with oxygen-free nitrogen. The mixture was allowed to react at room temperature, with occasional mixing, for several days. Toluene

Table	15.	Bond	angles	for	all	skeletal	atoms	of	the	two	enantiomers	of	the	oxide	of	the
					rea	arrangerr	nent pr	odu	ct 1	2 (de	$(a)^{a}$					

Atoms	Angle	Atoms	Angle
C(1) - P(1) - O(1)	114.4(4)	C(22) - C(21) - P(1)	119.9(8)
C(7) - P(1) - O(1)	116.5(4)	C(26) - C(21) - P(1)	116.5(8)
C(7) - P(1) - C(1)	102.6(5)	C(32) - C(31) - C(1)	118.7(9)
C(21) - P(1) - O(1)	113.8(4)	C(36) - C(31) - C(1)	120.3(9)
C(21) - P(1) - C(1)	101.3(5)	C(42) - C(41) - C(4)	117.8(9)
C(21) - P(1) - C(7)	106.6(4)	C(46) - C(41) - C(4)	120.8(9)
C(101) - P(101) - O(101)	117.3(5)	C(102) - C(101) - P(101)	121.0(8)
C(107) - P(101) - O(101)	113.2(4)	C(131) - C(101) - P(101)	115.3(7)
C(107) - P(101) - C(101)	105.2(4)	C(131) - C(101) - C(102)	123.6(9)
C(121)—P(101)—O(101)	113.5(4)	C(103) - C(102) - C(101)	124.4(9)
C(121) - P(101) - C(101)	102.3(5)	C(104) - C(103) - C(102)	105.5(8)
C(121) - P(101) - C(107)	103.9(4)	C(108) - C(103) - C(102)	117.0(8)
C(2) - C(1) - P(1)	120.3(8)	C(108) - C(103) - C(104)	104.6(8)
C(31) - C(1) - P(1)	116.0(7)	C(105) - C(104) - C(103)	111.0(9)
C(31) - C(1) - C(2)	123.7(9)	C(141) - C(104) - C(103)	118.9(9)
C(3) - C(2) - C(1)	123.9(10)	C(141) - C(104) - C(105)	129.6(10)
C(4) - C(3) - C(2)	107.6(8)	C(106) - C(105) - C(104)	113.1(9)
C(8) - C(3) - C(2)	116.3(8)	C(109) - C(105) - C(104)	125.3(10)
C(8) - C(3) - C(4)	103.2(8)	C(109) - C(105) - C(106)	121.5(9)
C(5) - C(4) - C(3)	111.9(8)	C(107) - C(106) - C(105)	118.5(8)
C(41) - C(4) - C(3)	122.4(9)	C(108) - C(106) - C(105)	103.3(8)
C(41)-C(4)-C(5)	124.9(9)	C(108) - C(106) - C(107)	59.1(6)
C(6) - C(5) - C(4)	111.5(8)	C(111) - C(106) - C(105)	114.4(8)
C(9) - C(5) - C(4)	125.7(9)	C(111) - C(106) - C(107)	124.6(8)
C(9) - C(5) - C(6)	122.4(8)	C(111) - C(106) - C(108)	122.2(8)
C(7) - C(6) - C(5)	116.8(8)	C(106) - C(107) - P(101)	118.8(7)
C(8) - C(6) - C(5)	103.8(8)	C(108) - C(107) - P(101)	119.0(7)
C(8) - C(6) - C(7)	59.5(6)	C(108)—C(107)—C(106)	59.7(6)
C(11) - C(6) - C(5)	114.5(8)	C(113)—C(107)—P(101)	113.4(7)
C(11) - C(6) - C(7)	125.4(8)	C(113)—C(107)—C(106)	117.2(8)
C(11) - C(6) - C(8)	123.1(8)	C(113) - C(107) - C(108)	118.6(8)
C(6) - C(7) - P(1)	119.9(6)	C(106) - C(108) - C(103)	107.2(8)
C(8) - C(7) - P(1)	119.6(7)	C(107)—C(108)—C(103)	116.9(8)
C(8) - C(7) - C(6)	60.4(6)	C(107) - C(108) - C(106)	61.2(6)
C(13)-C(7)-P(1)	113.4(7)	C(115) - C(108) - C(103)	117.0(9)
C(13) - C(7) - C(6)	117.1(8)	C(115) - C(108) - C(106)	121.3(9)
C(13) - C(7) - C(8)	116.7(8)	C(115)— $C(108)$ — $C(107)$	120.5(8)
C(6) - C(8) - C(3)	109.2(8)	C(122) - C(121) - P(101)	117.3(8)
C(7) - C(8) - C(3)	116.8(8)	C(126) - C(121) - P(101)	121.9(8)
C(7) - C(8) - C(6)	60.1(6)	C(132) - C(131) - C(101)	118.0(9)
C(15)-C(8)-C(3)	116.7(8)	C(136) - C(131) - C(101)	119.6(9)
C(15) - C(8) - C(6)	121.4(8)	C(142) - C(141) - C(104)	118.4(9)
C(15)-C(8)-C(7)	120.2(8)	C(146) - C(141) - C(104)	121.2(9)

"Estimated standard deviations are given in parentheses. Mean phenyl carbon – carbon–carbon bond angle and standard deviation was 119.9(12)°, range 116.8°-123.5(10-15)°. Range of carbon-oxygencarbon and carbon-carbon-oxygen bond angles was 105.5°-125.9(8-10)°.

(100 mL) was added and the mixture filtered to yield 2.63 g of yellow crystals, mp 162-165°C, which was confirmed to be the yellow adduct 6. A second crop of crystals, which were red (0.76 g), mp 197–199°C, was obtained on cooling the mother liquor. This was identified as the red adduct 8.

The filtrate from the red crystals was then chromatographed on Merck Kieselgel 60 (70-230 mesh ASTM) using diethyl ether as eluent. The first 100 mL fraction yielded 120 mg of clear crystals of the acetylene tetramer 9, identified by IR. Evaporation of the second 100 mL fraction gave colourless crystals, 279 mg, mp 187-191°C, identified by IR as dimethyl 3,6-diphenylphthalate 3. The third 100 mL fraction yielded 0.881 g of red crystals of 8, mp 193-199°C. This fraction was combined with the red adduct 8 recovered by crystallization (0.76 g) and recrystallized from 10 mL of toluene to yield 0.312 g of pure material, mp 197–199°C.

Rearrangement of the yellow adduct 6

(a) By literature method

The adduct 6 (112 mg) was dissolved in 50 mL of chloroform and refluxed for 3 h according to the published method (5). The solvent was removed under reduced pressure and the residue crystallized from 95% ethanol to yield 79 mg of yellow crystals, mp and mixture mp with starting material 163-165°C, and confirmed by ¹H NMR. A second crop of 27.5 mg of impure yellow crystals was mostly the rearrangement product 11 by ¹H NMR. The samples were combined (107 mg) in 50 mL of 1,2-dichloroethane and refluxed for 5 h. Crystallization of the evaporation residue as before gave 98 mg of colourless crystals of the rearrangement product 11, mp 183-185.5°C. This was identified as tetramethyl 2,3,6-triphenyl-2-phospha(III)tricyclo[6.5.0^{1,8}.0^{5,9}]-nona-3,6-diene-1,7,8,9-tetracarboxylate, compound 11, via an X-ray structure

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TABLE 16. Intermolecular distances of less than 3.4 Å from the crystal structure of the two enantiomers of the oxide of the rearrangement product, 12 (Å)^{*a*}

Atoms	Distance	Sym	T_x	 T _y	T_z
$\overline{\mathbf{C}(133)\cdots\mathbf{O}(2)}$	3.355	3	0	-1	-1
$C(25) \cdots O(2)$	3.318	4	0	Ō	Ō
$C(112) \cdots O(4)$	3.344	1	1	0	0
$C(114) \cdots O(6)$	3.254	4	1	-1	0
$C(32) \cdots O(7)$	3.395	1	1	0	0
$C(33) \cdots O(7)$	3.295	1	1	0	0
$C(12) \cdots O(9)$	3.238	1	-1	0	0
$O(104) \cdots C(12)$	3.394	1	1	0	0
$O(106) \cdots C(14)$	3.334	4	0	-1	0
$C(124) \cdots O(104)$	3.394	4	1	-1	0
$C(112) \cdots O(109)$	3.340	1	1	0	0

"The symmetry positions are for the second atom. They are defined: $2 = -x, -y, \frac{1}{2} + z; 3 = x, \frac{1}{2} - y, \frac{1}{2} + z; 4 = -x, \frac{1}{2} + y, z$. A negative symmetry position denotes inversion. The translations (*T*) are applied finally.

determination carried out on crystals of the oxide of this compound produced under mild conditions (see below).

(b) By improved modification

A solution of the yellow adduct 6 (1.013 g) in 100 mL of 1,2dichloroethane was boiled under reflux for 12 h. Progress of the reaction was followed by thin-layer chromatography (Polygram silica gel G, UV 254) using 5% acetone - 95% toluene for development. When the reaction was complete colourless crystals of the rearrangement product 11 (0.731 g) were isolated as described above, mp 210–213°C. UV (95% EtOH) λ_{max} nm (log ϵ): 201 (4.80), 248 (4.39). IR (KBr) cm⁻¹: 3030w, 3010w, 2955w, 2840w, 1750-1710s, 1640w, 1600w, 1485w, 1430s, 1375w, 1320m, 1230s, 1200s, 1120w, 1105w, 1060w, 945w, 850w, 815w, 760m, 700m, 640w, 520w. ¹H NMR (360 MHz) ppm: aromatic/olefinic protons 7.54–6.9; triplet centered at 6.4, J_{PH} 8.83, J_{HH} 8.76; doublet centered at 4.85, J_{HH} 8.45; ester methyl protons 3.82, 3.75, 3.68, 2.89. ¹³C NMR (360 MHz) ppm: carbonyl carbons 168.8, 167.1, 166.2, and 163.6; primary carbon (CH) 53 (DEPT 90°); quaternary carbon 47.6 J_{PC} 38.5 Hz; quaternary carbon 49.5, J_{PC} 20.5 Hz; quaternary carbon 40, J_{PC} 2.6 Hz (DEPT 135°); ester methyl carbons 51.6, 51.9, 52.7, 53.1, peak positions (relative intensities) for aromatic and olefinic carbons, some overlap and some coupled to phosphorus 152.2 (1.3), 145.5 (1.0), 145.3 (1.3), 141.0 (1.1), 140.9 (1.2), 136.8 (0.55), 133.9 (2.1), 132.7 (1.1), 132.6 (1.1), 129.7 (2.9), 129.6 (3.0), 129.5 (4.7), 128.8 (5.9), 128.2 (0.76), 128.1 (1.2), 128.0 (13.1), 127.9 (10.8), 127.8 (10.8), 127.7 (4.2), 127.6 (2.7), 127.32 (5.8), 127.25 (5.9), 126.6 (4.8). Decoupled ³¹P NMR, ppm: -34.8 SR (standard reference) 85% ortho phosphoric acid. Mass spectrum (relative intensity) calcd. for $C_{34}H_{29}O_8P$: 596, ¹³C satellite 597(38); found: methane negative ion CI (probe temp. 280° C): M⁻, 596(100); (M⁻) + 1, 597(37); methane CI (probe temp. >350°C), M + 1, 597.

Oxidation of the rearranged yellow adduct

The rearranged yellow adduct **11** (0.602 g) was dissolved in 50 mL of a 30:70 mixture of ethyl acetate and 95% ethanol, then 3.5 mL of 30% hydrogen peroxide was added. The mixture was refluxed for 7 h after which 25 mL of water was added and the organic solvent removed from the mixture by evaporation under reduced pressure. The residual aqueous phase was extracted with chloroform (3 × 50 mL), and the combined chloroform extracts were reduced in volume and ethyl acetate added. Colourless crystals of the oxide of the rearrangement product (0.312 g, mp 251–254°C), for which structure **12** was established later, were obtained from this solution. UV (95%EtOH) λ_{max} nm (log ϵ): 202 (4.66), 268 (4.18). IR (KBr) cm⁻¹: 3030m, 3010m, 2955w, 2840w,

1750–1705s, 1640m, 1600w, 1485w, 1430s, 1375m, 1320w, 1250–1230s, 1200s, 1120m, 1105w, 1060m, 945m, 850w, 815w, 760s, 700s, 640w, 520m. ¹H NMR (360 and 250 MHz) ppm: aromatic/olefinic protons 8.2–6.85; doublet of doublets centered at 4.72, $J_{\rm HH}$ 8.20 Hz, $J_{\rm PH}$ 1.82 Hz; methyl ester protons 3.86, 3.75, 3.69, 2.99. ¹³C NMR given in next preparation. ³¹P–¹H coupled NMR (360 MHz): appears as a doublet of triplets $J_{\rm PH1}$ 12.9 Hz, $J_{\rm PH2}$ 12.9 Hz, $J_{\rm PH3}$ 30.8 Hz. Decoupled ³¹P NMR 12.6 ppm, standard reference 85% ortho phosphoric acid. Mass spectrum (relative intensity) calcd. for $C_{34}H_{29}O_9P$: 612, ¹³C satellite 613(38); found: methane negative ion CI (probe temp. 350°C) M⁻, 612(100); (M⁻) + 1,613(39).

X-ray quality crystals from the oxide of the rearranged yellow adduct, 12

The title compound 12 (0.312 g) was crystallized from 20 mL of warm ethyl acetate to yield 0.219 g of colourless crystals, mp 252-254°C, too small for X-ray. X-ray quality crystals of the product were obtained from a low-recovery recrystallization from ethyl acetate, mp 252-254°C, on which an X-ray structure determination established that this was tetramethyl 2,3,6-triphenyl-2phosphatricyclo[6.1.0^{1.8}.0^{5.9}]-2-oxonona-3,6-diene-1,7,8,9-tetra-carboxylate, compound **12**. ¹³C NMR (360 MHz) ppm: carbonyl carbons 167.5, 166.1, 163.2, 165.0, J_{PC} 4.8 Hz; methine carbon 51.7, J_{PC} 13.1 Hz; tertiary carbons at 53.9, J_{PC} 3.3 Hz; 52.4, J_{PC} 3.3 Hz; 52.3; 45.5, J_{PC} 75.1 Hz; ester methyl carbons at 53.3, 52.9, 52.1, and 52.0; peak positions (relative intensities) for aromatic and olefinic carbons, some overlap and some coupled to phosphorus 156.6 (1.3), 145.8 (3.1), 140.9 (1.2), 139.9 (1.0), 137.2 (1.3), 137.1 (1.2), 133.3 (2.3), 132.8 (1.2), 131.6 (1.3), 131.49 (2.9), 131.47 (2.9), 130.3 (1.0), 129.82 (0.7), 129.76 (0.7), 129.6 (1.0), 129.4 (1.0), 128.9 (4.8), 128.1 (16.0), 127.8 (5.0), 127.6 (1.0), 126.9 (5.7), 126.8 (5.0).

Effect of alcoholic carbonate on oxide of rearrangement product, 12

A small sample of the oxide of the rearrangement product, **12**, was dissolved in 10 mL of 95% EtOH and 0.5 g of K_2CO_3 was added. During warming the solution colour changed from the initial colourless to purplish pink. Crystallization from ethyl acetate after removal of the potassium carbonate produced white crystals with different NMR properties than the starting material: decoupled ³¹P NMR (250 MHz) ppm: 19.8, SR 85% ortho phosphoric acid; ¹H NMR (250 MHz) ppm: aromatic and olefinic protons, 7.52–7.09; aromatic or olefinic proton centered at 6.57 (possible doublet of doublets), J_1 34.55 Hz, J_2 3.69 Hz; methine proton centered at 4.34, J 21.162 Hz; ester methyl protons at 3.77, 3.66, 3.55, and 2.98.

X-ray crystallography

The crystals of all three compounds gave well-defined extinctions between crossed polars. Crystals were mounted in glass Lindemann tubes, and Weissenberg and precision photography using Cu K_a radiation was used to determine unit cells and space groups, in all cases at 20°C. The experimental parameters and crystal data for all three compounds are given in Table 4. In all cases scattering factors for uncharged atoms were used (21). Supplementary material, (Tables S1–S8), including complete bond length and angle data and hydrogen atom fractional atomic coordinates where determined, anisotropic temperature parameters, and observed and calculated structure factors for all three crystals, has been deposited.⁴

⁴This supplementary material can be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A OS2, Canada.

Tables of hydrogen atom coordinates and bond lengths and angles have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Data collection and processing for yellow adduct 6

The crystal was found to be triclinic, space group P1 (No. 2), and approximate unit cell dimensions were established. The unit cell and matrix were refined using 25 2 θ measurements in the range 24-41°, each measured in both the positive and negative directions. Intensity measurements were made in the 20 range, 0.1°-45° from hkl = -11, 0, -13 to 11, 12, 12. Three standard orientation reflections 0,0,9; 6,0,0; and 0,8,0 were measured every 400 reflections. The standard intensity reflections were 5, 2, -4; 6, -1, -2;and 5, -5,0, also measured every 3600 seconds of X-ray time. The measurements were corrected for absorption, using an empirical absorption correction on the Nonius ($\mu = 0.86 \text{ cm}^{-1}$), then the EMPABS program⁵ was run on the mainframe computer. The phase problem was solved by direct methods. All atoms, including H, were found for the main molecule. Methyl hydrogens on acetone were calculated using AFIX in the SHELX program.⁶ The refinements converged with a maximum shift/e.s.d. (non-H) of 0.04 and the final difference map had a maximum of 0.21 e Å⁻³ and a minimum of 0.12 e Å⁻³, indicating that nothing had been missed. The final residuals were R = 0.0453, $R_w = 0.0453$, for 537 parameters and 2880 independent observations. Results are given in Tables 5-8.

X-ray data collection and processing for the red 2:1 adduct 8

This crystal was monoclinic, space group $P2_1/c$ (No. 14), and approximate unit cell dimensions were established. The unit cell and matrix were refined using 20 2 θ measurements in the range 12°– 36°, each measured in both the positive and negative directions. Intensity measurements were made in the 2 θ range, 0.1°–45° from hkl = -14,0,0 to 14,15,18 at 20°C. The scanning was in 200 steps of 0.01° in 2 θ counting for 0.25 s/step with background counting for 25 s at each end of the scan. Three standard orientation and intensity reflections 0,6,0; 0,0,6; and 6,0,0 were measured before every 50 reflections and were corrected for absorption using ABSB02 ($\mu = 0.98$ cm⁻¹) as an absorption correction.⁷

The phase problem was solved by MULTAN.⁸ Phosphorus and all carbon and oxygen atoms were found for the main molecule and for the cocrystallized ethanol. Ethanol was slightly disordered. Distance C52-O53 was DFIX'd at 2.15. The poor ethanol angle was not resolvable by crystallography, and this kept the *R*-value high. The refinement converged with a maximum shift/e.s.d.(non-H) of 0.128 (ethanol) and 0.023 otherwise. The final difference map had a maximum of 0.67 e Å⁻³ and a minimum of 0.15 e Å⁻³, and indicated that nothing had been missed. The final residuals were R = 0.0916, $R_w = 0.0937$, for 400 parameters and 2052 independent observations. Results are given in Tables 9–12.

X-ray data collection and processing for the oxide of the rearrangement product 12

This crystal was orthorhombic, space group $Pbc2_1$ (No. 29). Approximate unit cell dimensions and other data are given in Table 4. The unit and cell matrix were refined using 25 2 θ measurements in the range 40°-64°, each measured in both the positive and negative directions. Intensity measurements were made in the 2 θ range, 0°-130° from hkl = 0,0,0 to 9,26,35 at 20°C. Three stan-

dard orientation reflections 4,0,0; 0,0,16; and 0,12,0 were measured before every 400 reflections. The standard intensity reflections were the same three reflections, also measured every 3600 seconds of X-ray time, approximately every 50 reflections. The measurements were corrected for absorption using an empirical absorption correction, on the Nonius ($\mu = 12.5 \text{ cm}^{-1}$), then the EMPABS program (22) was run on the mainframe computer. The phase problem was solved by SHELXS Patterson methods. Because two molecules made up the asymmetric unit, all carbons could not be made anisotropic due to the SHELX-76 limitations on the number of parameters, so the six phenyl rings were left isotropic. Only four hydrogens were sought and refined (those on C2, C3, C102, and C103). We did not look for or calculate phenyl or methyl hydrogens. The refinements converged with a maximum shift/e.s.d. of 0.07, including the four located hydrogens. The final difference map had a maximum of 0.61 e $Å^{-3}$ and a minimum of 0.22 e Å⁻³, and indicated that nothing had been missed. The final residuals were R = 0.0747, $R_w = 0.0757$, for 321 parameters and 3255 independent observations. Results are given in Tables 13-16.

Summary

As has been found with the reaction of dimethyl acetylenedicarboxylate with N-substituted pyrroles (23) and with furans (e.g., refs. 24, 25), the adducts of this ester with 1,2,5triphenylphosphole are complex and similarly varied. We found few, if any, direct equivalencies in mode of reaction to the phosphorus heterocycle as compared to those observed for the nitrogen and oxygen heterocycles. The X-ray structure component of this work unequivocally confirms the cyclopropane-containing structure 6 for the yellow 2:1 adduct of the acetylene ester, formerly deduced solely from derivatives and spectroscopically. We also correct the various previously assigned structures of the thermal rearrangement product of this yellow adduct to structure 11 and that of its oxide to 12, which both still contain cyclopropyl moieties. Finally, we isolated for the first time a red 2:1 adduct of the acetylene ester to phosphole and have established its structure to be the cyclopent-3-enone stabilized phosphorane 8. In this product the phosphole ring remains intact, the only example among the adducts isolated. Preparation, isolation, and full characterization of the several products of the reaction of acetylene ester with the phosphole under different conditions as described here should also dispel the impression given by the literature (e.g., ref. 19) that these two compounds do not react under normal conditions.

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- I.G.M. Campbell, R.C. Cookson, and M.B. Hocking. Chem. Ind. (London), 359 (1962).
- 2. K. Alder and H.F. Rickert. Annalen, 524, 180 (1936).
- A.C. Cope, A.C. Haven, Jr., F.L. Ramp, and E.R. Trumbull. J. Am. Chem. Soc. 74, 4867 (1952).
- I.G.M. Campbell, R.C. Cookson, M.B. Hocking, and A.N. Hughes. J. Chem. Soc. 2184 (1965).
- 5. A.N. Hughes and S. Uaboonkul. Tetrahedron, 24, 3437 (1968).
- 6. N.E. Waite and J.C. Tebby. J. Chem. Soc. (C), 386 (1970).
- 7. M.B. Hocking. Can. J. Chem. 44, 1581 (1966).
- W.P. Ozbirn, R.A. Jacobsen, and J.C. Clardy. Chem. Commun. 1062 (1971).

⁵An empirical absorption correction program for the Nonius diffractometer. The absorption correction is measured as a function of χ for a conveniently placed reflection, and the experimental curve is used to correct other reflections. For details see ref. 22 and the Nonius CAD4 manual.

⁶G.M. Sheldrick and E. Egert. A program for crystal structure determination. Anorganisch-Chemisches Institut der Universitat Gottingen, Tammannstr. 4, 3400 Gottingen, Germany.

⁷P. Coppens, L. Leiserowitz, and D. Rabinovich. A program for the correction of crystallographic data for absorption. Modified to deal with the axis system on the University of Victoria Picker Diffractometer by G. Bushnell.

⁸P. Coppens, L. Leiserowitz, and D. Rabinovich. A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data.

- E. Winterfeldt and G. Giesler. Angew. Chem. Int. Ed. Engl. 5, 579 (1966).
- 10. R. Gericke and E. Winterfeldt. Tetrahedron, 27, 4109 (1971).
- 11. J.C. Kauer and H.E. Simmons. J. Org. Chem. 33, 2720 (1968).
- 12. E. LeGoff and R.B. LaCount. Tetrahedron Lett. 2333 (1967).
- L.D. Quin, N.S. Rao, R.J. Topping, and A.T. McPhail. J. Am. Chem. Soc. 108, 4519 (1986).
- L.D. Quin, E.D. Middlemas, and N.S. Rao. J. Org. Chem. 47, 905 (1982).
- N.E. Waite, D.W. Allen, and J.C. Tebby. Phosphorus, 1, 139 (1971).
- N.E. Waite, J.C. Tebby, R.S. Ward, M.A. Shaw, and D.H. Williams. J. Chem. Soc. (C), 1620 (1971).
- O. Kennard, W.D.S. Motherwell, and J.C. Coppola. J. Chem. Soc. (C), 2461 (1971).

- N.E. Waite, J.C. Tebby, R.S. Ward, and D.H. Williams. J. Chem. Soc. (C), 1100 (1969).
- A.N. Hughes, K. Amornraksa, S. Phisithkul, and V. Reutrakul. J. Heterocycl. Chem. 13, 65 (1976).
- 20. J.K. Stille, J.L. Eichelberger, J. Higgins, and M.E. Freeburger. J. Am. Chem. Soc. 94, 4761 (1972).
- D.T. Cromer and J.T. Waber. *In* International tables for X-ray crystallography. Vol. IV. *Edited by* J.A. Ibers and W.C. Hamilton. Kynoch Press, Birmingham. 1974.
- A.C.T. North, D.C. Phillips, and F.S. Mathews. Acta. Crystallogr. Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr. A24, 351 (1968).
- R.M. Acheson and N.F. Elmore. Adv. Heterocycl. Chem. 23, 264 (1978).
- 24. A.W. McCulloch, D.G. Smith, and A.G. McInnes. Can. J. Chem. 51, 4125 (1973).
- 25. J.D. Slee and E. LeGoff. J. Org. Chem. 35, 3897 (1970).