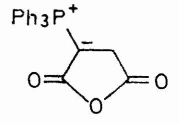
Structural Investigations of Ylides. Part VI.† Crystal and Molecular Structures of Two Resonance-stabilized Wittig Reagents 2-Carboxy-1-methoxycarbonylethyltriphenylphosphorane and its t-Butyl Ester

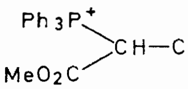
By **A. Forbes Cameron,* Fergus D. Duncanson,** and **Andrew A. Freer,** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

Victor W. Armstrong and **Robert Ramage,** Department of Organic Chemistry, University of Liverpool, Liverpool L69 3BX

The structures of the title compounds (3) and (4) have been determined by three-dimensional *X*-ray analyses by use of 3356 (3) and 2883 (4) independent reflexions measured by diffractometer. Crystals of both compounds are monoclinic, space group $P2_1/n$; for (3) $Z = 4$, unit cell dimensions $a = 8.579(1)$, $b = 13.893(4)$, $c = 16.768(3)$ Å, $\beta = 97.31(3)$; for (4), $Z = 4$, cell dimensions $a = 15.731(5)$, $b = 11.941(2)$, $c = 13.194(2)$ Å, $\beta = 97.22(1)$°. The structure of (3) was solved by the heavy-atom method, and of (4) by the symbolic addition method. Both structures have been refined by least-squares calculations to *R* 0.054 (3) and 0.076 (4). The results show that the structures are stabilised in part by delocalisation of the formal negative charge on the P^+–C^- group into the carbomethoxy-function.

IN 1963, Hudson and Chopard[1] prepared the ylide (1) by reaction of triphenylphosphine with maleic anhydride. Subsequent methanolysis of (1) produced a monomethyl ester which could plausibly be assigned either of the two structures (2) or (3), although the i.r. carbonyl absorptions exhibited by the product at 1730 and 1620 cm^{-1} were originally attributed to the carbomethoxy and carboxylate functions present in (2). There is now, however, considerable evidence that the alternative structure (3) is the more appropriate of the two possibilities. Thus phosphoranes such as (5) exhibit i.r. absorption at 1 620 cm^{-1} due to extensive delocalisation of the ester function with the ylide moiety. On this basis, consideration of the structure (3) would suggest that the 1 730 cm^{-1} absorption may be derived from a carboxy-function. Moreover, the corresponding diester (4), synthesised by standard methods, and for which a form comparable to (2) is not possible, also exhibits i.r. absorptions at 1 730 and 1 620 cm^{-1}.


(1)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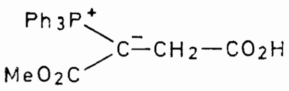
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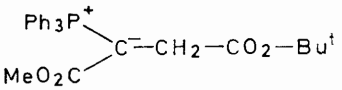
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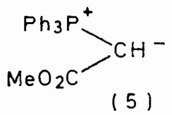
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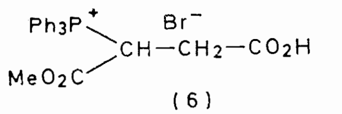
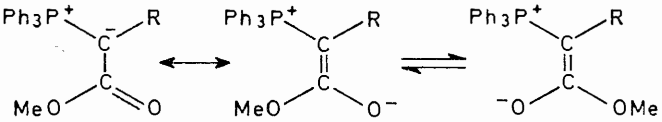

(6)

Further support for (3) as opposed to (2) derives from an analysis of the ^{1}H n.m.r. spectrum, which reveals a methylene group coupled to a β-^{31}P as a doublet (*J* 15 Hz), whereas in (2) the methylene would be expected to show a more complex ABRX system resulting from coupling with both the α-C*H* and β-^{31}P of the type exhibited by the phosphonium salt (6). Moreover, the ^{1}H n.m.r. spectra of (3) and (4) are similar, which would not be expected from comparison of (2) and (4). Low-temperature ^{1}H n.m.r. studies also agree with earlier findings[2] of restricted rotation in resonance-stabilised Wittig reagents, which results from partial double-bond character between the ylide-carbon and the carbonyl-carbon [*e.g.* (7)↔(8)⇄(9)]. In the case of (4), the two rotameric isomers corresponding to (8) and (9) may be resolved ~ −30 °C.


(7) (8) (9)

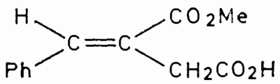

(10)

TABLE 1

^{13}C Chemical shifts and one-bond ^{13}C–^{31}P nuclear spin couplings of the ylide carbon atoms

Ylide	*J*(CP) [a]	δ^{13}C [b]
(1)	135	33.9
(3)	90	39.0
(4)	130	36.0

[a] In Hz, accurate to ±2.5 Hz. [b] In p.p.m. with respect to internal [^{13}C]tetramethylsilane, accurate to ±0.1 p.p.m.

^{13}C N.m.r. spectra of the ylides (1), (3), and (4) (Table 1) show the ylide-carbon to be strongly shielded, thus indicating carbanion character at this centre.[3] Finally, in keeping with structure (3), the ylide reacted efficiently with benzaldehyde to afford the acid (10) by a Wittig reaction.

The foregoing spectroscopic and chemical evidence has been confirmed by three-dimensional *X*-ray analyses of

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† Part V, A. F. Cameron and A. A. Freer, *Acta Cryst.*, 1974, **B30**, 2696.

[1] R. F. Hudson and P. A. Chopard, *Helv. Chim. Acta*, 1963, **46**, 2178.

[2] H. J. Bestmann, G. Joachim, and I. Lengyel, *Tetrahedron Letters*, 1966, 3355.

[3] G. A. Grey, *J. Amer. Chem. Soc.*, 1973, **95**, 5092.

(3) and (4). These latter studies not only provide details of the molecular geometries which indicate that in both molecules there is considerable delocalisation from the ylide-carbon into the methoxycarbonyl function, but also allow comparison of the same ylide system in two crystal environments.

EXPERIMENTAL

Synthetic and Spectroscopic.—^{1}H N.m.r. spectra were measured for $CDCl_3$ solutions on a Varian HA 100, and ^{13}C n.m.r. spectra on a Varian XL 100 15FT with tetramethylsilane as internal standard. $^{13}C-^1H$ couplings were eliminated by broad-band ^{1}H noise-modulated decoupling. Chemical shift data are quoted in p.p.m. downfield from tetramethylsilane.

Triphenylphosphoranylidenesuccinic Anhydride, (1). This was prepared by the method of ref. 1. M.p. 169 °C; ^{13}C n.m.r. ($CDCl_3$) δ 33.9 (d, *J* 135 Hz), 37.0 (d, *J* 13 Hz), 124.3 (d, *J* 93 Hz), 129.7 (d, *J* 13 Hz), 133.7 (m), 168.0 (d, *J* 10 Hz), and 175.2 (d, *J* 10 Hz).

2-*Carboxy*-1-*methoxycarbonylethyltriphenylphosphorane*, (3). This was prepared by the method of ref. 1. M.p. 144 °C; ^{1}H n.m.r. ($CDCl_3$) δ 2.89 (2H; d, *J* 15.5 Hz), 3.34 (3H; S), 7.3—7.9 (15H; m), 9.09 (H; br s); ^{13}C n.m.r. ($CDCl_3$) δ 31.0 (br s, $W_{\frac{1}{2}}$ 10 Hz), 38.6 (d, *J* 90 Hz), 123.4 (d, *J* 90 Hz), 129.8 (d, *J* 13 Hz), 134.2 (m), 171.6 (d, *J* 8 Hz), and 174.0 (d, *J* 7 Hz).

1-*Methoxycarbonyl*-2-t-*butoxycarbonylethyltriphenylphosphorane*, (4). Butyl bromoacetate (3.9 g, 20 mmol) was added to a solution of (5) (13.36 g, 40 mmol) in anhydrous ethyl acetate (150 ml) under nitrogen. The solution was heated under reflux for 4 h, then cooled. Evaporation of the filtrate afforded (4), crystallised from ethyl acetate–hexane as prisms, m.p. 140—142 °C (6.75 g, 75%); $\nu_{max.}$ ($CHCl_3$) 1 730, 1 620 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 1.32 (9H; 5), 2.89 (2H; d, *J* 17 Hz), 3.34 (3H; S), 7.50 (15H; m); ^{13}C n.m.r. ($CDCl_3$) δ 29.0 (s), 34.0 (d, *J* 12 Hz), 36.0 (d, *J* 130 Hz), 49.6 (s), 79.2 (s), 128.1 (d, *J* 90 Hz), 129.0 (d, *J* 12 Hz), 132.1 (s), 134.3 (d, *J* 10 Hz), 171.3 (s), 175.1 (s) (Found: C, 72.35; H, 6.8. $C_{27}H_{29}O_4P$ requires C, 72.31; H, 6.52%).

3-*Methoxycarbonyl*-4-*phenylbut*-3-*enoic Acid*, (10).—Benzaldehyde (9.4 g; 89 mmol) was added to a solution of (3) (34.8 g; 89 mmol) in anhydrous dimethyl sulphoxide–tetrahydrofuran (1 : 1, 280 ml) under nitrogen, and left at room temperature for 7 days. After dilution with water (1 l) and acidification to pH 3, the solution was extracted with ether. The ethereal solution was extracted with saturated sodium hydrogen carbonate solution. The aqueous solution was acidified then extracted with chloroform. After drying (anhydrous sodium sulphate) the chloroform was removed *in vacuo* to give an oil (17.5 g) which was chromatographed over silica (500 g). Elution with 2% methanol in chloroform gave the acid (10) (15.1 g, 77%), crystallised from benzene–hexane as needles, m.p. 79 °C; $\nu_{max.}$ 2 500—3 000, 1 725, 1 705, and 1 640 cm^{-1}; $\lambda_{max.}$ (MeOH) 269 nm (ε 14 400); ^{1}H n.m.r. ($CDCl_3$) δ 3.46 (2H; S), 3.80 (3H; S), 7.32 (5H; S), 7.88 (H; S), 11.66 (H; S) (Found: C, 65.43; H, 5.45. $C_{12}H_{12}O_4$ requires C, 65.43; H, 5.48%).

Crystallographic.—*Crystal Data*, (3), $C_{23}H_{21}PO_4$, M = 392.4, Monoclinic, a = 8.579(1), b = 13.893(4), c = 16.768(3) Å, β = 97.31(3)°, U = 1 978.9 Å^3, D_m = 1.41 (by flotation), Z = 4, D_c = 1.34, $F(000)$ = 824. Space group $P2_1/n$ (C^5_{2h}) from systematic absences. Mo-K_α *X*-radiation, λ = 0.7107 Å, μ(Mo-K_α) = 1.71 cm^{-1}.

(4), $C_{27}H_{29}PO_4$, M = 448.5, Monoclinic, a = 15.731(5), b = 11.941(2), c = 13.194(2) Å, β = 97.22(1)°, U = 2 458.8 Å^3, D_m = 1.20 (by flotation), Z = 4, D_c = 1.21, $F(000)$ = 942. Space group $P2_1/n$ (C^5_{2h}) from systematic absences. μ(Mo-K_α) = 1.47 cm^{-1}.

TABLE 2

Atomic parameters

(*a*) Fractional co-ordinates for (3) (×10^5 for P; ×10^4 for other atoms)

	x/*a*	*y*/*b*	*z*/*c*
P	20 565(13)	15 535(8)	19 719(6)
O(1)	4 861(4)	−550(2)	1 632(2)
O(2)	4 362(4)	330(2)	2 713(2)
O(3)	3 949(5)	1 404(3)	143(2)
O(4)	3 180(4)	120(3)	−588(2)
C(1)	2 732(5)	547(3)	1 511(2)
C(2)	4 028(5)	67(3)	1 910(3)
C(3)	5 936(7)	154(6)	3 101(4)
C(4)	2 195(5)	267(3)	650(3)
C(5)	3 212(6)	671(3)	56(3)
C(6)	956(5)	1 311(3)	2 805(3)
C(7)	926(6)	380(4)	3 112(3)
C(8)	147(6)	203(4)	3 773(3)
C(9)	−591(6)	947(5)	4 125(3)
C(10)	−591(6)	1 870(4)	3 813(3)
C(11)	169(6)	2 065(4)	3 143(3)
C(12)	710(5)	2 207(3)	1 239(3)
C(13)	1 195(7)	3 030(4)	872(4)
C(14)	170(9)	3 495(5)	285(4)
C(15)	−1 344(8)	3 130(5)	75(4)
C(16)	−1 824(7)	2 304(5)	434(3)
C(17)	−798(6)	1 844(4)	1 020(3)
C(18)	3 675(5)	2 347(3)	2 348(3)
C(19)	3 754(6)	2 824(4)	3 092(3)
C(20)	5 073(6)	3 382(4)	3 365(3)
C(21)	6 301(6)	3 449(4)	2 908(4)
C(22)	6 222(6)	2 978(4)	2 176(3)
C(23)	4 920(6)	2 423(4)	1 894(3)

(*b*) Anisotropic temperature factors * (Å^2 ×10^4) for (3)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	287	266	251	−6	34	−5
O(1)	516	381	432	117	195	−10
O(2)	394	476	312	116	22	−8
O(3)	968	515	387	−272	237	−50
O(4)	554	518	319	−37	112	−86
C(1)	365	289	269	−4	58	−23
C(2)	402	309	326	−12	123	18
C(3)	440	1 174	546	242	−118	−11
C(4)	415	392	291	−47	71	−62
C(5)	413	371	262	68	15	19
C(6)	305	365	275	−9	45	−28
C(7)	426	370	359	−13	80	5
C(8)	523	555	393	−62	89	97
C(9)	454	787	311	−34	96	32
C(10)	423	670	421	79	102	−162
C(11)	377	434	402	45	71	−72
C(12)	384	341	293	54	6	−125
C(13)	549	484	567	−6	−49	188
C(14)	853	619	652	95	−42	269
C(15)	721	805	439	332	−98	24
C(16)	447	737	448	127	−66	−109
C(17)	385	512	432	35	−5	−25
C(18)	330	272	351	−16	8	−9
C(19)	426	487	376	−51	43	−77
C(20)	483	554	494	−98	8	−141
C(21)	387	487	617	−104	−31	−92
C(22)	384	530	591	−110	126	−93
C(23)	430	434	423	−95	107	−104

Mean estimated standard deviations (Å^2 × 10^4)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	5	5	5	5	4	4
O	24	20	18	18	16	15
C	25	26	25	22	25	22

TABLE 2 (*Continued*)

(*c*) Fractional co-ordinates for (4) ($\times 10^5$ for P; $\times 10^4$ for other atoms)

	x/*a*	*y*/*b*	*z*/*c*
P	75 754(9)	85 297(10)	3 112(8)
O(1)	6 351(3)	11 320(3)	−196(3)
O(2)	6 268(3)	9 607(3)	−927(3)
O(3)	8 661(3)	11 351(4)	71(3)
O(4)	8 311(3)	12 492(3)	1 307(3)
C(1)	7 279(4)	9 892(4)	482(3)
C(2)	6 609(4)	10 356(4)	−206(4)
C(3)	5 591(7)	9 971(8)	−1 634(7)
C(4)	7 734(4)	10 669(4)	1 258(4)
C(5)	8 283(4)	11 526(4)	789(4)
C(6)	6 786(4)	7 479(4)	549(4)
C(7)	5 947(4)	7 777(5)	607(4)
C(8)	5 359(4)	6 977(6)	790(5)
C(9)	5 587(5)	5 970(6)	934(5)
C(10)	6 422(5)	5 562(5)	869(6)
C(11)	7 017(5)	6 349(4)	674(5)
C(12)	8 514(3)	8 243(4)	1 231(3)
C(13)	9 335(4)	8 475(5)	1 010(4)
C(14)	10 023(5)	8 321(6)	1 755(5)
C(15)	9 891(5)	7 967(5)	2 711(5)
C(16)	9 088(5)	7 752(5)	2 946(4)
C(17)	8 402(4)	7 893(4)	2 216(4)
C(18)	7 855(4)	8 260(4)	−966(4)
C(19)	7 610(5)	7 282(6)	−1 506(5)
C(20)	7 806(5)	7 167(8)	−2 507(6)
C(21)	8 219(5)	7 985(7)	−2 949(5)
C(22)	8 451(5)	8 951(7)	−2 422(5)
C(23)	8 253(5)	9 092(5)	−1 436(4)
C(24)	8 847(4)	13 442(5)	1 046(4)
C(25)	9 763(6)	13 097(8)	1 192(8)
C(26)	8 536(7)	13 832(7)	−25(5)
C(27)	8 664(5)	14 311(5)	1 829(5)

(*d*) Anisotropic temperature factors * (Å^2 $\times$ 10^4) for (4)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	620	334	345	52	62	4
O(1)	1 206	691	750	−226	551	−253
O(2)	809	408	499	−43	134	−63
O(3)	1 171	396	605	232	71	81
O(4)	883	475	494	86	−70	16
C(1)	727	404	443	−41	44	−8
C(2)	757	533	471	70	148	−1
C(3)	650	800	677	−34	223	57
C(4)	965	628	742	−210	71	29
C(5)	1 035	423	884	−67	−34	63
C(6)	827	421	836	2	66	37
C(7)	696	367	380	18	78	16
C(8)	722	688	484	15	203	27
C(9)	705	857	617	−16	138	30
C(10)	765	661	571	18	−24	29
C(11)	949	583	406	34	109	90
C(12)	775	446	478	−1	129	71
C(13)	655	509	397	108	72	−30
C(14)	961	671	624	−75	166	−196
C(15)	938	1 036	636	−43	109	−429
C(16)	864	1 193	426	125	106	−175
C(17)	1 112	811	503	45	311	−21
C(18)	1 090	599	441	105	211	−24
C(19)	891	322	377	4	90	24
C(20)	820	418	424	27	161	−20
C(21)	667	454	484	17	98	−57
C(22)	866	473	508	−89	64	−24
C(23)	822	908	1 140	28	185	−256
C(24)	1 312	643	577	−159	−19	73
C(25)	871	467	635	−50	−34	−75
C(26)	802	367	427	−10	168	50
C(27)	1 300	705	854	77	−465	22

Mean estimated standard deviations (Å^2 $\times$ 10^4)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	8	6	6	6	5	5
O	25	20	21	20	21	17
C	30	27	22	23	21	20

TABLE 2 (*Continued*)

(*e*) Hydrogen atom fractional co-ordinates for (3) ($\times 10^3$)

	x/*a*	*y*/*b*	*z*/*c*
H(4)	385(7)	29(5)	−83(4)
H(31)	552(7)	23(5)	299(4)
H(32)	602(7)	45(4)	371(4)
H(33)	656(7)	33(5)	283(4)
H(7)	133(7)	−14(4)	287(3)
H(8)	8(6)	−54(4)	402(3)
H(9)	−139(6)	86(4)	47(3)
H(10)	−133(7)	234(4)	407(3)
H(11)	3(6)	281(4)	281(3)
H(13)	212(7)	331(5)	87(4)
H(14)	82(8)	416(5)	−6(4)
H(15)	−195(8)	349(5)	−32(4)
H(16)	−275(7)	200(4)	33(3)
H(17)	−123(6)	129(4)	129(3)
H(19)	287(7)	275(4)	346(3)
H(20)	507(6)	376(4)	390(3)
H(21)	719(6)	383(4)	306(3)
H(22)	722(6)	300(4)	181(3)
H(23)	501(7)	209(4)	135(4)

(*f*) H-atom fractional co-ordinates for (4) ($\times 10^3$)

	x/*a*	*y*/*b*	*z*/*c*
H(31)	559(4)	1 077(7)	−179(5)
H(32)	526(5)	968(7)	−179(7)
H(33)	576(4)	945(6)	−241(5)
H(41)	732(5)	1 102(6)	169(6)
H(42)	820(5)	1 030(6)	181(6)
H(7)	577(4)	854(7)	57(5)
H(8)	482(5)	714(6)	90(5)
H(9)	520(4)	525(6)	113(5)
H(10)	661(4)	482(7)	88(5)
H(11)	757(5)	621(6)	64(6)
H(13)	938(4)	870(6)	38(6)
H(14)	1 052(5)	846(6)	154(5)
H(15)	1 040(5)	789(6)	319(6)
H(16)	892(5)	755(6)	352(6)
H(17)	791(5)	780(6)	236(6)
H(19)	726(4)	671(6)	−123(5)
H(20)	759(4)	646(6)	−283(5)
H(21)	850(4)	793(6)	−361(6)
H(22)	876(4)	947(6)	−272(5)
H(23)	842(4)	979(6)	−1 079(5)
H(251)	1 016(5)	1 370(6)	107(5)
H(252)	1 001(5)	1 281(7)	169(6)
H(253)	1 001(5)	1 271(6)	63(6)
H(261)	796(5)	1 399(7)	−16(6)
H(262)	866(4)	1 329(6)	−58(6)
H(263)	877(4)	1 457(7)	−9(5)
H(271)	899(4)	1 404(6)	255(6)
H(272)	897(4)	1 498(7)	175(5)
H(273)	813(5)	1 441(6)	174(6)

* Thermal parameters are the values of U_{ij} in the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^{*}\cdot c^{*} + 2U_{31}lhc^{*}\cdot a^{*} + 2U_{12}hka^{*}\cdot b^{*})]$.

Crystallographic measurements. Cell parameters of compounds were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α (λ = 1.5418 Å) radiation, and from precession photographs taken with Mo-K_α (λ = 0.7107 Å) radiation, and were later refined by least-squares techniques.

Intensity measurements were made on a Hilger and Watts Y 290 computer-controlled diffractometer with Zirconium filtered Mo radiation, and the θ—ω scan technique in the range 2θ 0—54°. Small crystals of both compounds mounted about *b* produced 3 356 for (3) and 2 883 independent reflexions for (4) [having $I \geqslant 3\sigma(I)$]. Both sets of intensities were corrected for Lorentz and polarisation factors, but absorption effects were considered small and were ignored.

Structure determinations and refinements. The structure of (3) was resolved by the conventional heavy-atom method, using initially the phasing appropriate to the phosphorus position. The complete structure was revealed in the course of two rounds of structure-factor and electron-density calculations. After each structure-factor calculation, in which an overall isotropic thermal parameter (U_{iso} 0.05 Å^2) was assumed, data were placed on an approximate absolute scale by equating $k\,\Sigma|F_o|$ and $\Sigma|F_c|$.

The structure of (4) was resolved by application of the symbolic addition method, an initial E map based on 270 reflexions with $|E| \geqslant 1.79$ clearly revealing the 20 non-hydrogen atoms of the triphenylphosphine group and the adjacent carbon atom. A structure-factor and electron-density calculation based on these 20 atomic positions then revealed the complete structure.

TABLE 3

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bonded distances

	(3)	(4)
P–C(1)	1.732(4)	1.715(5)
P–C(6)	1.813(4)	1.817(5)
P–C(12)	1.818(5)	1.823(5)
P–C(18)	1.821(4)	1.823(5)
C(1)–C(2)	1.392(6)	1.415(7)
C(1)–C(4)	1.509(6)	1.495(7)
C(2)–O(1)	1.243(6)	1.221(6)
C(2)–O(2)	1.388(5)	1.366(6)
C(3)–O(2)	1.442(7)	1.394(11)
C(4)–C(5)	1.512(6)	1.520(8)
C(5)–O(3)	1.197(6)	1.198(7)
C(5)–O(4)	1.321(5)	1.338(6)
C(24)–O(4)		1.480(7)
C(24)–C(25)		1.489(11)
C(24)–C(26)		1.510(9)
C(24)–C(27)		1.518(8)

Mean C–C for phenyl rings:

(3)	(4)
1.390(8)	1.382(9)

(*b*) Interbond angles

	(3)	(4)
C(1)–P–C(6)	115.4(2)	115.5(3)
C(1)–P–C(12)	108.7(2)	107.5(2)
C(1)–P–C(18)	111.1(2)	112.9(2)
C(6)–P–C(12)	105.4(2)	105.7(2)
C(6)–P–C(18)	107.1(2)	106.5(2)
C(12)–P–C(18)	108.8(2)	108.3(3)
P–C(1)–C(2)	117.7(2)	118.7(2)
P–C(1)–C(4)	123.8(2)	124.4(3)
C(2)–C(1)–C(4)	117.6(3)	116.7(3)
C(1)–C(2)–O(1)	127.7(3)	125.7(4)
C(1)–C(2)–O(2)	113.1(3)	112.7(3)
O(1)–C(2)–O(2)	119.2(3)	121.6(3)
C(2)–O(2)–C(3)	117.3(3)	117.5(5)
C(1)–C(4)–C(5)	113.8(3)	112.7(3)
C(4)–C(5)–O(3)	125.1(3)	124.7(4)
C(4)–C(5)–O(4)	111.7(3)	110.8(4)
O(3)–C(5)–O(4)	123.2(3)	124.5(4)
C(5)–O(4)–C(24)		121.7(4)
O(4)–C(24)–C(25)		109.2(5)
O(4)–C(24)–C(26)		109.1(4)
O(4)–C(24)–C(27)		101.7(4)
C(25)–C(24)–C(26)		113.7(6)
C(25)–C(24)–C(27)		111.3(5)
C(26)–C(24)–C(27)		111.1(5)
P–C(6)–C(7)	119.5(2)	120.8(3)
P–C(6)–C(11)	119.7(2)	120.9(3)
P–C(12)–C(13)	120.7(2)	121.3(2)
P–C(12)–C(17)	119.0(2)	119.3(3)
P–C(18)–C(19)	122.7(2)	122.4(3)
P–C(18)–C(23)	117.4(2)	118.0(3)

Mean C–C–C for phenyl rings:

(3)	(4)
120.0(4)	120.0(5)

TABLE 3 (*Continued*)

(*c*) Selected intramolecular non-bonded distances $\leqslant$3.80 Å

	(3)	(4)
P · · · O(2)	2.77	2.78
P · · · O(3)	3.65	3.80
O(1) · · · C(4)	2.87	2.82
O(1) · · · C(5)	3.30	3.16
C(6) · · · O(2)	3.24	3.24
C(6) · · · C(2)	3.63	3.57
C(7) · · · O(2)	3.10	3.06
C(7) · · · C(1)	3.27	3.30
C(7) · · · C(2)	3.56	3.46
C(12) · · · O(3)	3.69	>4.00
C(12) · · · C(4)	3.19	3.15
C(13) · · · O(3)	3.59	3.76
C(17) · · · C(1)	3.52	3.61
C(17) · · · C(4)	3.48	3.65
C(18) · · · O(2)	2.91	2.97
C(18) · · · C(2)	3.27	3.41
C(19) · · · O(2)	3.57	3.62
C(23) · · · O(2)	3.28	3.33
C(23) · · · O(3)	3.27	3.37
C(23) · · · C(1)	3.23	3.26
C(23) · · · C(2)	3.36	3.56

(*d*) Intermolecular distances for (3) <3.80 Å *

C(3) · · · C(9$^{\mathrm{I}}$)	3.42	O(4) · · · C(5$^{\mathrm{III}}$)	3.30
C(8) · · · C(8$^{\mathrm{I}}$)	3.64	C(5) · · · C(5$^{\mathrm{III}}$)	3.61
C(22) · · · C(16$^{\mathrm{I}}$)	3.67	C(10) · · · O(3$^{\mathrm{IV}}$)	3.33
C(22) · · · C(17$^{\mathrm{I}}$)	3.74	O(4) · · · C(21$^{\mathrm{V}}$)	3.44
C(22) · · · C(11$^{\mathrm{I}}$)	3.78	O(4) · · · C(20$^{\mathrm{V}}$)	3.65
C(21) · · · C(10$^{\mathrm{I}}$)	3.63	C(15) · · · C(19$^{\mathrm{V}}$)	3.59
O(4) · · · C(16$^{\mathrm{II}}$)	3.58	C(14) · · · C(3$^{\mathrm{VI}}$)	3.77
O(4) · · · C(17$^{\mathrm{II}}$)	3.43	C(22) · · · C(8$^{\mathrm{VI}}$)	3.60
O(1) · · · O(3$^{\mathrm{III}}$)	3.47	C(21) · · · C(7$^{\mathrm{VI}}$)	3.60
O(1) · · · O(4$^{\mathrm{III}}$)	2.64	C(20) · · · C(4$^{\mathrm{VI}}$)	3.77
O(1) · · · C(5$^{\mathrm{III}}$)	3.46	C(20) · · · C(7$^{\mathrm{VI}}$)	3.74
O(3) · · · O(4$^{\mathrm{III}}$)	3.26	C(10) · · · O(1$^{\mathrm{VI}}$)	3.73
O(4) · · · O(4$^{\mathrm{III}}$)	3.49	C(11) · · · O(1$^{\mathrm{VI}}$)	3.33
O(4) · · · C(2$^{\mathrm{III}}$)	3.47	O(1) · · · C(21$^{\mathrm{VII}}$)	3.56

* Roman numeral superscripts refer to the following equivalent positions, relative to that of the reference molecule at x, y, z:

I $1 + x, y, z$
II $-x, -y, -z$
III $1 - x, -y, -z$
IV $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
V $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
VI $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
VII $\frac{3}{2} - x, -\frac{1}{2} - y, \frac{1}{2} - z$

(*e*) Intermolecular distances for (4) <3.90 Å

C(27) · · · C(10$^{\mathrm{I}}$)	3.89	C(4) · · · C(10$^{\mathrm{IV}}$)	3.85
C(27) · · · C(11$^{\mathrm{I}}$)	3.73	C(16) · · · C(10$^{\mathrm{IV}}$)	3.83
C(9) · · · C(9$^{\mathrm{II}}$)	3.56	C(27) · · · C(7$^{\mathrm{IV}}$)	3.82
C(15) · · · C(3$^{\mathrm{III}}$)	3.74	O(1) · · · C(20$^{\mathrm{V}}$)	3.60
O(1) · · · C(16$^{\mathrm{IV}}$)	3.57	O(1) · · · C(21$^{\mathrm{V}}$)	3.29
O(4) · · · C(17$^{\mathrm{IV}}$)	3.55		

* Roman numeral superscripts refer to the following equivalent positions:

I $x, 1 + y, z$
II $1 - x, 1 - y, -z$
III $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$
IV $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
V $\frac{3}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$

The positional, vibrational, and overall-scale parameters for both structures were refined by three-dimensional least-squares calculations, which for (3) converged after 11 cycles when R was 0.054 and R' ($= \Sigma w\Delta^2/\Sigma w|F_o|^2$) was 0.006. The introduction of anisotropic vibrational parameters in cycle 5 necessitated the use of the block-diagonal approximation to the normal-equation matrix in this and subsequent cycles. A difference synthesis evaluated after the fourth cycle of refinement revealed all the hydrogen-atom positions, and contributions from these atoms were initially included without refinement from cycle 5 onwards, but were refined (constant U_{iso} 0.05 Å^2) in the last two cycles.

Refinement of (4) converged after 16 cycles, when R was 0.076 and R' 0.012, the general refinement strategy paralleling that of (3). Hydrogen-atom positions were again located from difference syntheses evaluated after the isotropic refinement, and were included initially without refinement being refined (constant U_{iso} 0.05 Å^2) in the last five cycles.

Fractional co-ordinates and thermal parameters for both compounds are given in Table 2, while Table 3 contains bond lengths, interbond angles, and pertinent intra- and inter-molecular non-bonded distances; estimated standard deviations are derived from the least-squares procedures and are best regarded as minimum values. For (3), the mean σ for P–C, C–O, and C–C bonds are 0.004, 0.006, and 0.008 Å, while for valency angles σ is 0.3°. The corresponding values for (4) are 0.005, 0.007, and 0.009 Å, and 0.4°.

TABLE 4

Equations of least-squares planes in the form $lX + mY + nZ = d$, where X, Y, and Z are co-ordinates in Å with respect to an orthogonalised axial system. Deviations (Å) of relevant atoms from the planes are given in square brackets

(*a*) For (3)

Plane (1): C(6)—(11)

$$-0.7684X' - 0.1991Y' - 0.6082Z' = -3.3566$$

[C(6) −0.012, C(7) 0.005, C(8) 0.007, C(9) −0.011, C(10) −0.002, C(11) 0.012, P −0.098]

Plane (2): C(12)—(17)

$$-0.4320X' + 0.5606Y' + 0.7064Z' = 3.0232$$

[C(12) 0.002, C(13) −0.001, C(14) −0.004, C(15) 0.007, C(16) −0.004, C(17) −0.000, P −0.077]

Plane (3): C(18)—(23)

$$0.3768X' - 0.8025Y' + 0.4625Z' = 0.1897$$

[C(18) −0.003, C(19) 0.004, C(20) −0.004, C(21) 0.003, C(22) −0.002, C(23) 0.002, P 0.100]

Plane (4): P, C(1), C(2), C(4)

$$0.7152X' + 0.5956Y' - 0.3657Z' = 1.0451$$

[P 0.001, C(1) −0.067, C(2) 0.026, C(4) 0.027, O(2) −0.161, O(1) 0.238]

Dihedral angles (°) between planes: (1)–(2) 102.1, (1)–(3) 114.3, (2)–(3) 106.6

(*b*) For (4)

Plane (1): C(6)—(11)

$$-0.1025X' - 0.1555Y' - 0.9825Z' = -3.1702$$

[C(6) −0.003, C(7) −0.004, C(8) 0.008, C(9) −0.006, C(10) 0.000, C(11) 0.005, P −0.030]

Plane (2): C(12)—(17)

$$-0.1219X' + 0.9502Y' + 0.2867Z' = 8.2173$$

[C(12) −0.009, C(13) 0.009, C(14) −0.003, C(15) −0.002 C(16) 0.001, C(17) 0.004, P 0.132]

Plane (3): C(18)—(23)

$$-0.8431X' + 0.4097Y' - 0.3484Z' = -6.0582$$

[C(18) −0.014, C(19) 0.005, C(20) 0.004, C(21) −0.004, C(22) −0.006, C(23) 0.014, P 0.085]

Plane (4): P, C(1), C(2), C(4)

$$0.7232X' + 0.2807Y' - 0.6310Z' = 11.1726$$

[P 0.010, C(1) −0.032, C(4) 0.011, C(2) 0.011, O(2) 0.005, O(1) 0.031]

Dihedral angles (°) between planes: (1)–(2) 1146, (1)–(3) 111.4, (2)–(3) 113.1

Details of least-squares planes calculated for various portions of the molecular framework are given in Table 4. The atomic numbering schemes are shown in Figures 1 and 2.

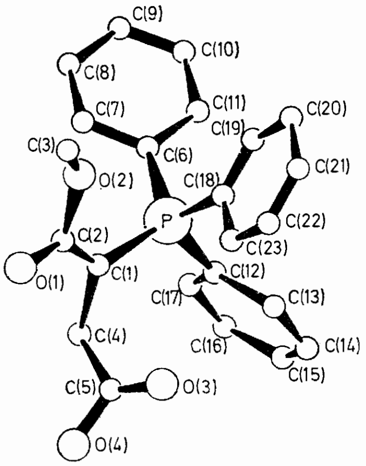


FIGURE 1 One molecule of (3) showing the atom numbering system used. Hydrogen atoms are numbered as the atoms to which they are bonded

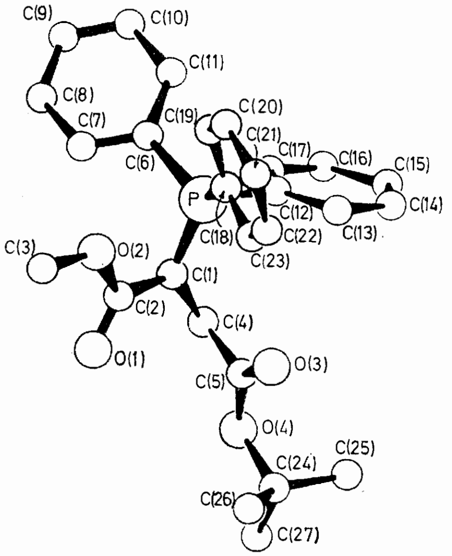


FIGURE 2 One molecule of (4) showing the atom numbering system used. Hydrogen atoms are numbered as the atoms to which they are bonded

DISCUSSION

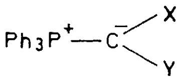
That the X-ray analysis of 2-carboxy-1-methoxycarbonylethyltriphenylphosphorane confirms the assignation of molecular structure (3) as opposed to (2), is evidenced by the location of the hydrogen atom bonded to O(4) of the acid group, and by the hydrogen bonding between the acid grouping and the carbomethoxy moiety of neighbouring molecules [O(4) ··· O(1) 2.64 Å]. This evidence is supported by the near-trigonal geometry of C(1), and by the dimensions of the acid group in which the lengths of the C(5)–O(3) [1.197(6) Å] and C(5)–O(4) [1.321(5) Å] bonds are identical to the corresponding bonds [1.198(7) and 1.338(6) Å] in (4).

In addition to confirming the predictions of molecular structure made on the bases of spectroscopic and chemical evidence, the *X*-ray analyses of (3) and (4) together provide an opportunity to study in detail the molecular geometry of the class of stabilised ylide $\geqslant\overset{+}{P}-\overset{-}{C}R-CO_2Me$ in different crystallographic environments. The most striking difference between them emerges from a comparison of their conformations. Examination of their corresponding torsion angles (Table 5) reveals that whereas P–C(1)–C(2)–O(2) is 14.7(5)° for (3), it is 1.3(6)° in (4), while for the closely related torsion angle P–C(1)–C(2)–O(1), the respective values are −165.9(4) and −177.5(4)°. Although it might otherwise be expected that the group of atoms $P^+-C^--C=O$ should be planar for efficient delocalisation, other examples containing this group of atoms also show small deviations from planarity. Thus in (11b),[4] (11c),[5] and (12),[6] the corresponding torsion angles are respectively 12, 4.8, and 8°. It is possible that the conformational differences between (3) and (4) may result from the different packing environments, since the crystal structure of (3) exhibits considerably more intermolecular contacts <3.80 Å than does (4). Moreover, the crystal structure of (3) is also characterised by the previously mentioned O(4) · · · O(1) hydrogen bond, which directly involves the carbonyl oxygen of the carbomethoxy-group. There is no parallel interaction in the crystal structure of (4). It is also plausible that the decreased ^{13}C and ^{31}P coupling in (3) (Table 1) may have a root in the 14.7(5)° torsion angle about its C(1)–C(2)–.

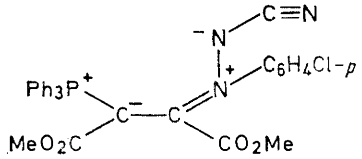
TABLE 5

Selected torsion angles (deg.)

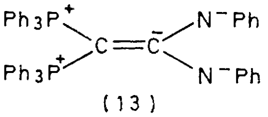
	(3)	(4)
P–C(1)–C(2)–O(2)	14.7(5)	1.3(6)
P–C(1)–C(2)–O(1)	−165.9(4)	−177.5(4)
C(4)–C(1)–C(2)–O(1)	3.3(7)	−2.8)8)
C(4)–C(1)–C(2)–O(2)	−175.9(4)	−175.9(4)
C(1)–C(4)–C(5)–O(3)	−28.4(7)	−34.4(7)
C(1)–C(4)–C(5)–O(4)	152.5(4)	147.8(4)
C(2)–C(1)–P–C(6)	−75.8(4)	−67.9(5)
C(2)–C(1)–P–C(12)	166.1(3)	174.3(4)
C(2)–C(1)–P–C(18)	46.4(4)	54.9(5)
C(4)–C(1)–P–C(6)	115.7(4)	117.8(5)
C(4)–C(1)–P–C(12)	−2.5(4)	0.1(5)
C(4)–C(1)–P–C(18)	−122.2(4)	−119.3(4)
C(1)–P–C(6)–C(7)	10.3(5)	14.9(5)
C(1)–P–C(6)–C(11)	−170.9(4)	−164.5(5)
C(1)–P–C(12)–C(13)	−101.9(4)	−87.0(5)
C(1)–P–C(12)–C(17)	75.0(4)	86.3(5)
C(1)–P–C(18)–C(19)	−139.8(4)	−139.2(5)
C(1)–P–C(18)–C(23)	35.8(4)	34.9(5)



	X	Y
(11) a;	H	H
b;	I	COPh
c;	Cl	COPh
d;	H	$SO_2C_6H_4Me$



(12)



(13)

$Ph_3P{=}C{=}PPh_3$

(14)

With the exception of the conformational differences, other features of the molecular geometries of (3) and (4) are identical. Thus in both molecules the $P^+-C^--C=O$ grouping adopts a *trans*-configuration about the C(1)–C(2) bond, the ylide-carbon C(1) possesses near-trigonal geometry, and the C(1)–C(2) bond [1.392(6) in (3), 1.415(7) Å in (4)] is considerably shortened. The carbonyl bonds [C(2)–O(1)] of the stabilising carbomethoxy-groups are in both cases slightly longer [1.243(6) in (3), 1.221(6) Å in (4)] than the corresponding bonds [C(5)–O(3)] of either the acid function of (3) [1.197(6) Å] or the t-butyl ester function of (4) [1.198(7) Å]. There are thus clear indications, in keeping with the spectroscopic evidence, of delocalisation of the formal negative charge on C(1) into the carbomethoxy-groups of the two molecules. Similar patterns of delocalisation are suggested by the lengths of 1.361(20) and 1.441(9) Å for the C^--CO bonds of (11c) and (12) respectively. In the case of (12) the length of the $C-CO_2Me$ bond not adjacent to the triphenylphosphine moiety is 1.507(9) Å, while the torsion angle for this bond is −69°.

The lengths of the P–C(1) bonds in (3) [1.732(4) Å] and (4) [1.715(5) Å] may be compared with those for (11c) [1.736(14) Å], (11d)[7] [1.709(19) Å], and (13)[8] [1.726(2) Å], which are considerably longer than for either (11a)[9] [1.662(8) Å] or (14)[10] [1.624 Å]. In the case of (11a), there is no possibility of stabilisation except by additional bonding between the phosphorus and ylide-carbon atom, while for (14) there is almost certainly a high degree of π-bond character in the central P–C bonds. Nevertheless, it seems likely that the lengths of the P^+-C^- bonds in (3), (4), and similar stabilised molecules, are consistent with at least some degree of π-bond character. Similar effects have been noted for the P^+-N^- bonds in stabilised ylides of the class $\geqslant P^+-N^--R$.[11]

Further features of the conformations of (3) and (4) are the approximately tetrahedral geometries of both phosphorus atoms. The three phosphorus-bonded phenyl rings are all planar, adopting the familiar ' propeller ' conformation, and the phosphorus atom lies slightly out of the plane of each ring. This effect has been noted for similar molecules.[11] Other dimensions within the molecules are as expected, and apart from

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those contacts already noted, there are no abnormally short intermolecular distances.

We thank Dr. Roy Lapper for ^{13}C n.m.r. spectra, and the S.R.C. and Eli Lily for the provision of a CAPS studentship (to V. W. A.). Crystallographic computations were performed on the Glasgow University KDF 9 using programs developed by the Glasgow group, and on the E.R.C.C. IBM 370/158 by use of the ' *X*-Ray '72 ' suite of programs.[12]

[4/1871 *Received, 12th September,* 1974]

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[12] ' *X*-Ray '72,' University of Maryland Technical Report TR 192, 1972.