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A Single-Crystal X-Ray Analysis of a Novel Intramolecular Hydrogen-Bonded Biphenyl Phosphorane

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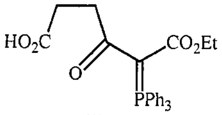
Abstract

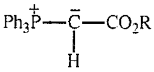
An X-ray crystal structure and ^{1}H n.m.r. analysis of the biphenyl phosphorane (4a) has revealed the presence of an intramolecular hydrogen bond resulting in an unusual biphenyl with a bridge forming a nine-membered ring. The related biphenyl phosphorane (4b) exists as two diastereoisomers.

Acylphosphoranes, e.g. (1), prepared from the reaction between a cyclic anhydride and the ylide (2a), are known to cyclize rapidly to give the corresponding enol lactones, e.g. (3).[1] The reaction of diphenic anhydride with ylide (2a) was studied in an attempt to extend this reaction to larger ring systems. The product phosphorane (4a) proved to be of particular interest in that it possessed an unusual intramolecular hydrogen bond which appeared to impart chirality.

^{13}C, ^{1}H and ^{31}P n.m.r. spectral data for (4a) were consistent with the proposed phosphorane structure.[1,2] In particular, the OCH_2CH_3 proton resonances occurred at characteristic upfield positions, δ 0·65 and 3·66. The ^{13}C chemical shifts and ^{13}C–^{31}P coupling constants for C(1), C(2), C(3) (numbering of Fig. 1) and the PPh_3 group are also characteristic of a phosphorane.

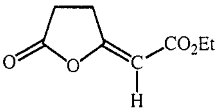


(1)

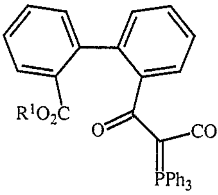


$Ph_3\overset{+}{P}-\underset{\displaystyle H}{\overset{-}{C}}-CO_2R$

(2a) R = Et
(2b) R = CH(Me)CH₂Me



(3)



	R^1	R^2
(4a)	H	Et
(4b)	H	$CH(Me)CH_2Me$
(5a)	Me	Et
(5b)	Me	$CH(Me)CH_2Me$

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[1] Abell, A. D., and Massy-Westropp, R. A., *Aust. J. Chem.*, 1982, **35**, 2077.
[2] Abell, A. D., Clark, B. M., and Robinson, W. T., *Aust. J. Chem.*, 1988, **41**, 1243.

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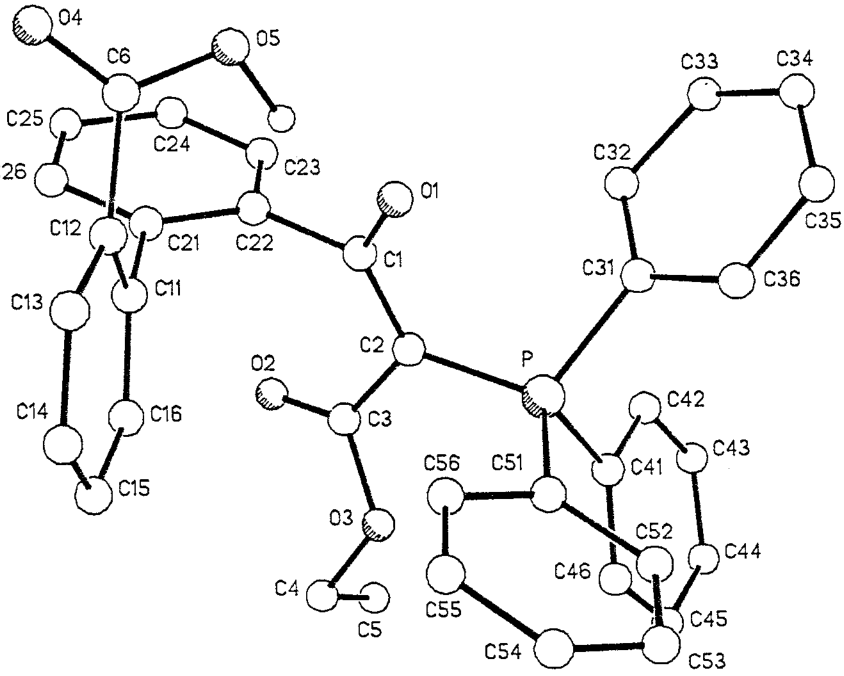

Fig. 1. Perspective view and atom labelling of the phosphorane (4a).

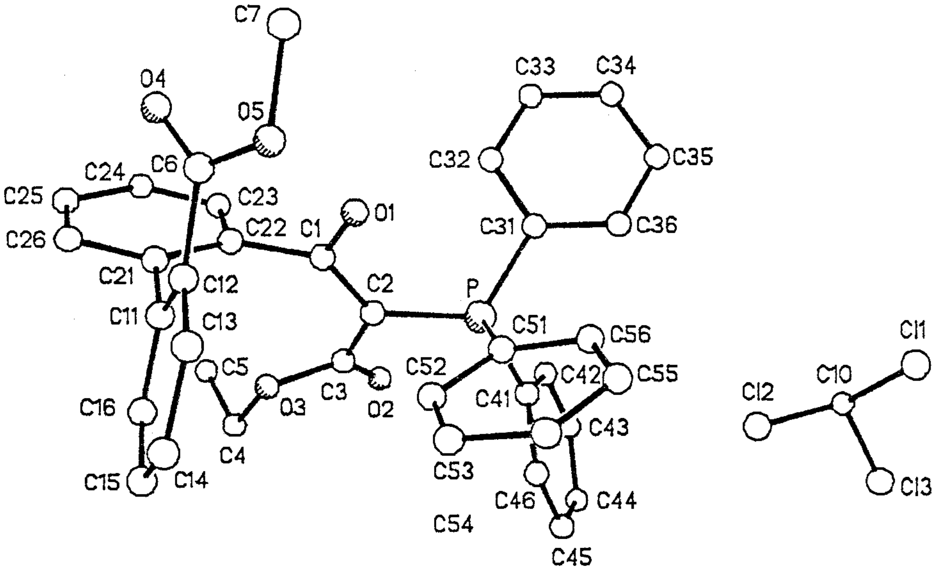

Fig. 2. Perspective view and atom labelling of the phosphorane (5a). Cocrystallization with chloroform is indicated.

The ^1H n.m.r. spectrum of (4a) in $CDCl_3$, and interestingly in CD_3OD, revealed that the signal at δ 3·66 ($OC\mathbf{H}_2CH_3$) was a complex multiplet that collapsed to an AB quartet on irradiation at δ 0·65 ($OCH_2C\mathbf{H}_3$). This observation suggested that the biphenyl had restricted rotation in solution most likely due to intramolecular hydrogen bonding. Consistent with this was the fact that the corresponding methylated biphenyl phosphorane (5a), which is incapable of hydrogen bonding while retaining the biphenyl 2,2′-substitution, gave a quartet for the $OC\mathbf{H}_2CH_3$ protons at δ 3·58. The monoethyl ester of diphenic acid, which is capable of hydrogen bonding, gave a clean quartet by ^1H n.m.r. at δ 4·03 ($OC\mathbf{H}_2CH_3$). A single-crystal X-ray analysis of (4a) and, for comparison, (5a) was undertaken in an attempt to establish hydrogen bonding in the crystalline state.

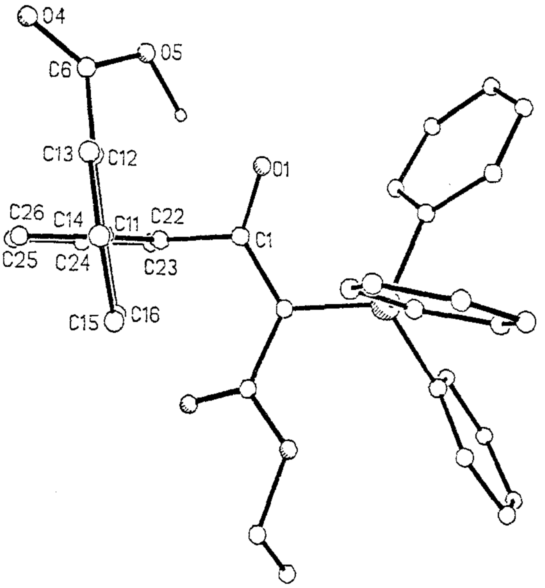

Fig. 3. Perspective view on (4a) showing biphenyl dihedral angle.

Perspective drawings of the phosphoranes (4a) and (5a), with atom labelling, are presented in Figs 1 and 2, respectively. Tables 1–3 list atomic coordinates and bond lengths and angles, with standard deviations in parentheses. The O(1)–H–O(5) angle in (4a) is 148·6°, and the critical O(1)· · ·O(5) distance is 2·67 Å, well within the accepted range for hydrogen bonding.[3] The resulting hydrogen bond forms an unusual nine-membered ring in a boat-like conformation. For comparison the O(1)· · ·O(5) distance in (5a) is 3·39 Å.

A number of other features of the molecular structure of (4a) are consistent with hydrogen bonding. The dihedral angle between the two phenyl rings in structure (4a) (Fig. 3) is unusually large[4] at 99·4°, and in the methylated structure (5a) the corresponding angle is 79·5°. The greater angle observed in (4a) is presumably a consequence of the intramolecular hydrogen bonding.

[3] Greenwood, N. N., and Earnshaw, A., 'Chemistry of the Elements' p. 65 (Pergamon: Oxford 1984).

[4] Leser, J., and Rabinovich, D., *Acta Crystallogr., Sect. B*, 1978, **34**, 2260, and references therein.

The biphenyl (5a) (Fig. 2) adopts the regular *syn* conformation reported for other biphenyls.[4]

A single-crystal X-ray analysis of the phosphorane (1)[2] revealed that the carbonyl group and the phosphorus of the triphenylphosphine group are 2·8° from planarity, and in (5a) the corresponding O(1)–C(1)–C(2)–P dihedral angle is −0·1°. The C(1) carbonyl of (4a), although still *syn* to phosphorus, is rotated 10·9° out of the plane of the delocalized system, a result that is also consistent with hydrogen bonding.

The phosphorane (4b) was similarly prepared from diphenic anhydride and racemic ylide (2b). Twinning of the ^{13}C and ^{1}H resonances was consistent

Table 1. Atom coordinates, and temperature factors (Å^2), for the phosphoranes (4a) and (5a)

Phosphorane (4a)					Phosphorane (5a)				
Atom	10^4x	10^4y	10^4z	10^3U_{eq}[A]	Atom	10^4x	10^4y	10^4z	10^3U_{eq}[A]
P	1958(3)	7961(1)	203(2)	19(1)	P	8350(1)	7677(1)	6421(1)	14(1)
O(1)	2441(6)	8113(2)	2518(4)	23(2)	O(1)	8453(2)	5823(2)	6837(2)	20(1)
C(1)	3233(8)	8406(3)	2009)6)	20(3)	O(2)	11111(2)	9856(2)	8246(2)	23(1)
C(2)	3106(8)	8441(3)	940(6)	16(3)	O(3)	10833(2)	9103(2)	9390(2)	21(1)
C(3)	3699(9)	8942(4)	443(7)	22(4)	O(4)	8377(2)	3889(2)	7797(2)	23(1)
O(2)	4707(6)	9233(2)	748(4)	30(2)	O(5)	6187(2)	3476(2)	6874(2)	27(1)
O(3)	3860(6)	9073(2)	−435(4)	28(2)	C(1)	9382(3)	6779(2)	7573(2)	15(1)
C(4)	3341(9)	9566(4)	−1008(5)	46(4)	C(2)	9553(3)	7855(2)	7556(2)	15(1)
C(5)	4277(9)	9371(4)	−1739(6)	63(5)	C(3)	10565(3)	9014(2)	8384(2)	16(1)
O(4)	1982(6)	9133(2)	5537(4)	38(3)	C(4)	11931(3)	10198(3)	10269(2)	28(1)
O(5)	2443(5)	8424(2)	4463(4)	26(2)	C(5)	13345(4)	10197(3)	10345(3)	44(2)
C(6)	2044(8)	8962(8)	4681(6)	30(4)	C(6)	7385(3)	4144(3)	7723(2)	22(1)
C(11)	2434(8)	9471(3)	3011(5)	15(2)	C(7)	6186(4)	2418(3)	6056(3)	34(2)
C(12)	1604(8)	9359(3)	3776(6)	21(2)	C(11)	8529(3)	6220(2)	9259(2)	19(1)
C(13)	243(9)	9625(5)	3725(6)	32(3)	C(12)	7312(3)	5186(3)	8576(2)	19(1)
C(14)	−227(9)	9964(3)	2902(6)	32(3)	C(13)	6030(3)	5106(3)	8741(3)	25(2)
C(15)	635(8)	10054(3)	2102(6)	27(3)	C(14)	5953(4)	6029(3)	9584(3)	32(2)
C(16)	1938(8)	9799(3)	2167(6)	21(2)	C(15)	7137(4)	7050(3)	10252(3)	33(2)
C(21)	3950(8)	9267(3)	3129(5)	13(2)	C(16)	8408(4)	7145(3)	10084(3)	29(2)
C(22)	4350(8)	8768(3)	2628(6)	18(2)	C(21)	9960(3)	6401(2)	9173(2)	17(1)
C(23)	5720(8)	8596(3)	2722(5)	24(2)	C(22)	10397(3)	6755(2)	8434(2)	16(1)
C(24)	6713(8)	8914(3)	3328(5)	25(3)	C(23)	11788(3)	7036(3)	8465(2)	19(1)
C(25)	6318(8)	9429(3)	3853(6)	23(2)	C(24)	12728(3)	6948(3)	9196(2)	23(1)
C(26)	4907(8)	9596(4)	3742(6)	23(2)	C(25)	12291(3)	6591(3)	9917(2)	25(1)
C(31)	2020(8)	7239(3)	767(5)	19(2)	C(26)	10925(3)	6338(3)	9916(2)	23(1)
C(32)	3287(9)	7034(4)	1242(5)	35(3)	C(31)	8636(3)	6957(2)	5150(2)	16(1)
C(33)	3341(9)	6439(4)	1590(6)	45(3)	C(32)	9628(3)	6476(2)	5108(2)	21(1)
C(34)	2155(10)	6106(4)	1513(7)	50(3)	C(33)	9884(3)	5969(3)	4147(3)	26(2)
C(35)	910(9)	6316(3)	1051(6)	36(3)	C(34)	9156(3)	5917(3)	3213(2)	26(1)
C(36)	829(8)	6883(3)	659(5)	22(2)	C(35)	8173(3)	6391(3)	3244(2)	25(1)
C(41)	2479(8)	7848(3)	−1067(5)	17(2)	C(36)	7924(3)	6923(2)	4208(2)	19(1)
C(42)	3612(8)	7479(3)	−1144(6)	29(3)	C(41)	8491(3)	9089(2)	6559(2)	14(1)
C(43)	4025(8)	7366(3)	−2129(6)	34(3)	C(42)	9510(3)	9703(2)	6352(2)	19(1)
C(44)	3322(8)	7609(3)	−2957(7)	36(3)	C(43)	9720(3)	10830(3)	6451(2)	25(1)
C(45)	2188(8)	7990(3)	−2862(6)	33(3)	C(44)	8932(3)	11359(3)	6960(2)	28(2)
C(46)	1810(8)	8119(3)	−1895(6)	27(3)	C(45)	7902(3)	10753(3)	7252(2)	27(2)
C(51)	157(8)	8203(3)	32(6)	20(2)	C(46)	7672(3)	9615(2)	7045(2)	20(1)
C(52)	−849(8)	7940(3)	−698(5)	26(2)	C(51)	6566(3)	6945(2)	6345(2)	15(1)
C(53)	−2252(9)	8123(4)	−742(6)	38(3)	C(52)	6311(3)	6948(2)	7276(2)	20(1)
C(54)	−2607(10)	8543(4)	−64(6)	43(3)	C(53)	4940(3)	6498(3)	7262(3)	24(1)
C(55)	−1666(8)	8794(4)	649(6)	40(3)	C(54)	3829(3)	6050(2)	6328(3)	24(1)
C(56)	−251(9)	8630(3)	706(6)	28(3)	C(55)	4078(3)	6027(2)	5395(2)	22(1)
					C(56)	5440(3)	6466(2)	5401(2)	19(1)
					Cl(1)	5272(1)	8777(1)	1940(1)	53(1)
					Cl(2)	7070(1)	10051(1)	4193(1)	53(1)
					Cl(3)	6365(1)	11311(1)	3114(1)	51(1)
					C(10)	6710(4)	10075(3)	2950(3)	36(2)

[A] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

with an equal mixture of two diastereoisomers. The ^{1}H n.m.r. spectrum was assigned on the basis of homonuclear decoupling experiments. Separation of the isomers by chromatography or crystallization was not possible; however, methylation of the mixture with diazomethane gave a single racemic product (5b) according to ^{1}H and ^{13}C n.m.r. spectroscopy. Again these results support intramolecular hydrogen bonding and hence restricted rotation in the biphenyl phosphoranes (4a,b).

Bridged biphenyl systems involving an intramolecular hydrogen bond are uncommon, and only a few crystal structures (e.g.[5,6]) have been reported. Interestingly, the crystal structure of diphenic acid[7] shows the two carboxylic acid groups are *anti*, and hence no intramolecular hydrogen bonding is

Table 2. Selected bond lengths (Å) for (4a) and (5a)

Atoms	(4a)	(5a)	Atoms	(4a)	(5a)
O(1)–C(1)	1·270(10)	1·246(2)	O(4)–C(6)	1·207(10)	1·206(4)
C(1)–C(2)	1·408(11)	1·431(5)	O(5)–C(6)	1·334(10)	1·345(3)
C(1)–C(22)	1·521(11)	1·505(5)	C(6)–C(12)	1·524(11)	1·491(4)
C(2)–C(3)	1·473(11)	1·449(3)	C(11)–C(12)	1·388(11)	1·407(3)
C(2)-P	1·769(7)	1·760(3)	C(11)–C(21)	1·526(10)	1·497(5)
C(3)–O(2)	1·208(10)	1·223(4)	C(21)–C(22)	1·399(11)	1·404(5)
C(3)–O(3)	1·367(10)	1·356(4)	C(31)–P	1·814(8)	1·808(3)
O(3)–C(4)	1·468(10)	1·455(3)	C(41)–P	1·831(8)	1·809(3)
C(4)–C(5)	1·472(12)	1·486(5)	C(51)–P	1·812(8)	1·813(3)

Table 3. Selected bond angles (degrees) for (4a) and (5a)

Atoms	(4a)	(5a)	Atoms	(4a)	(5a)
O(1)–C(1)–C(2)	125·4(7)	121·3(3)	C(3)–O(3)–C(4)	114·7(6)	116·5(2)
C(2)–C(1)–C(22)	118·8(7)	120·7(2)	O(4)–C(6)–O(5)	123·4(7)	123·0(3)
C(1)–C(2)–P	119·5(6)	113·7(2)	O(5)–C(6)–C(12)	116·2(7)	112·5(3)
C(2)–C(3)–O(2)	128·3(7)	126·6(3)	C(12)–C(11)–C(21)	119·9(6)	124·5(3)
O(2)–C(3)–O(3)	122·3(7)	121·3(2)	C(6)–C(12)–C(11)	123·6(7)	120·9(3)
O(3)–C(4)–C(5)	111·3(7)	111·8(3)	C(11)–C(12)–C(13)	119·3(7)	119·7(3)
O(4)–C(6)–C(12)	120·3(7)	124·4(2)	C(13)–C(14)–C(15)	120·1(8)	120·2(4)
C(16)–C(11)–C(21)	118·8(7)	117·1(2)	C(11)–C(21)–C(26)	117·4(7)	119·1(3)
C(6)–C(12)–C(13)	117·1(7)	119·3(2)	C(1)–C(22)–C(21)	118·9(7)	121·5(3)
C(12)–C(13)–C(14)	119·2(8)	120·5(2)	C(21)–C(22)–C(23)	120·7(7)	119·3(3)
C(14)–C(15)–C(16)	119·8(7)	119·7(2)	C(23)–C(24)–C(25)	120·4(7)	119·6(3)
C(11)–C(21)–C(22)	121·1(6)	121·4(3)	C(21)–C(26)–C(25)	119·0(7)	120·9(3)
C(22)–C(21)–C(26)	121·5(7)	119·1(3)	C(2)–P–C(31)	110·4(3)	114·0(2)
C(10–C(22)–C(23)	120·3(7)	119·2(3)	C(2)–P–C(41)	111·9(4)	110·4(1)
C(22)–C(23)–C(24)	119·6(7)	120·9(3)	C(31)–P–C(41)	104·4(4)	105·0(2)
C(24)–C(25)–C(26)	118·8(7)	120·2(3)	C(2)–P–C(51)	114·0(4)	110·6(2)
O(1)–C(1)–C(22)	115·8(7)	117·7(3)	C(31)–P–C(51)	108·6(4)	111·4(1)
C(1)–C(2)–C(3)	120·2(7)	125·9(3)	C(41)–P–C(51)	107·1(3)	104·9(1)
C(3)–C(2)–P	119·2(6)	120·5(30	C(6)–O(5)–C(7)		114·3(3)
C(2)–C(3)–O(3)	109·2(7)	112·0(3)			

[5] Ottersen, T., *Acta Chem. Scand., Ser. A*, 1977, **31**, 1, 480.

[6] Staab, H. A., Krieger, C., and Höne, M., *Tetrahedron Lett.*, 1988, **29**, 5629.

[7] Fronczek, F. R., Davis, S. T., Gehrig, L. M. B., and Gandour, R. D., *Acta Crystallogr., Sect. C*, 1987, **43**, 1615.

possible although intermolecular hydrogen bonding does occur. The biphenyl phosphoranes (4a,b) show a unique combination of intramolecular hydrogen bonding and sterically large biphenyl 2,2′-substitution. The bulky substituent on C(22) must provide a steric barrier to rotation about the biphenyl central bond, permitting the formation of the intramolecular hydrogen bond which subsequently hinders biphenyl rotation.

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Pye Unicam SP3-300 spectrometer. ^{1}H, ^{13}C and ^{31}P n.m.r. spectra were recorded on a Varian CFT300 spectrometer, in $CDCl_3$ solutions, downfield relative to Me_4Si (^{1}H and ^{13}C) and phosphoric acid (^{31}P). Light petroleum refers to the fraction of b.p. 60–70°.

Reactions with the Ylide (2a)

Diphenic anhydride (100 mg, 0·45 mmol) was refluxed with the ylide (2a) (144 mg, 0·42 mmol) in chloroform (5 ml) for 18 h. The solvent was removed under reduced pressure, and the resulting oil was crystallized from ethyl acetate/light petroleum to yield *2′-[2-(ethoxycarbonyl)-1-oxo-2-(triphenylphosphoranylidene)ethyl]-1,1′-biphenyl-2-carboxylic acid* (4a) as colourless crystals (72 mg, 28%), m.p. 205° (dec.) (Found: C, 75·4; H, 5·4. $C_{36}H_{29}O_5P$ requires C, 75·5; H, 5·5%). ν_{max} (KBr) 1740, 1700, 1670 cm^{-1}. ^{1}H n.m.r. δ ($CDCl_3$) 0·65, t, J 7·2 Hz, $OCH_2C\mathbf{H}_3$; 3·66, m, $OC\mathbf{H}_2CH_3$; 7·15–7·70, m, aromatic. ^{13}C n.m.r. δ ($CDCl_3$) 13·4, 59·5, 75·0 (d, J 108 Hz), 124·1 (d, J 93 Hz), 125·3, 127·3, 127·6, 128·0, 128·3, 128·7 (d, J 13 Hz), 129·3, 129·6, 132·3 (d, J 10 Hz), 136·1, 137·1, 138·7, 166·8 (d, J 15 Hz), 171·1, 192·8 (d, J 4 Hz). ^{31}P n.m.r. δ ($CDCl_3$) 17·82.

The phosphorane (4a) (50 mg, 0·09 mmol) in tetrahydrofuran was methylated with an excess of diazomethane. Evaporation under reduced pressure gave an oil. Crystallization from chloroform/light petroleum gave *methyl 2′-[2-(ethoxycarbonyl)-1-oxo-2-(triphenylphosphoranylidene)ethyl]-1,1′-biphenyl-2-carboxylate* (5a) (42 mg, 82%), m.p. 168–168·5° (Found: C, 65·2; H, 4·6. $C_{37}H_{31}O_5P.CHCl_3$ requires C, 64·7; H, 4·6%). ν_{max} (KBr) 1740, 1670, cm^{-1}. ^{1}H n.m.r. δ ($CDCl_3$) 0·53, t, J 7·2 Hz, $OCH_2C\mathbf{H}_3$; 3·46, s, OCH_3; 3·58, q, J 7·2 Hz, $OC\mathbf{H}_2CH_3$; 7·14–7·95, m, aromatic. ^{13}C n.m.r. δ ($CDCl_3$) 13·5, 51·7, 58·4, 72·4 (d, J 108 Hz), 126·2 (d, J 93·4 Hz), 126·3, 126·5, 126·6, 128·4 (d, J 12·6 Hz), 129·3, 130·0, 130·6, 131·0, 131·6 (d, J 2·8 Hz), 131·8, 133·3, (d, J 10·1 Hz), 137·9, 142·6, 143·4, 167·1 (d, J 15·6 Hz), 167·9, 192·8 (d, J 4·5 Hz). ^{31}P n.m.r. δ ($CDCl_3$) 17·94.

Relations with the Ylide (2b)

A solution of ylide (2b) (294 mg, 0·78 mmol) and diphenic anhydrride (175 mg, 0·78 mmol) in chloroform (25 ml) was refluxed for 3 h. Evaporation under reduced pressure gave an oil. Crystallization from ethyl acetate/light petroleum gave *2′-[2-(1-methylpropoxycarbonyl)-1-oxo-2-(triphenylphosphoranylidene)ethyl]-1,1′-biphenyl-2-carboxylic acid* (4b) (148·1 mg, 32%), m.p. 184–186° (Found: C, 75·7; H, 5·5. $C_{38}H_{32}O_5P$ requires C, 76·0; H, 5·5%). ν_{max} 3500, 3000, 2600, 1740, 1700 cm^{-1}. ^{1}H n.m.r. data revealed the presence of two diastereoisomers. ^{1}H n.m.r. δ ($CDCl_3$) 0·58, t, J 7·5 Hz, $(CH_2C\mathbf{H}_3)_A$; 0·63, d, J 6·5 Hz, $(CH_3)_A$; 0·67, t, J 7·4 Hz, $(CH_2C\mathbf{H}_3)_B$; 0·74, d, J 6·0 Hz, $(CH_3)_B$; 0·98, m, $(C\mathbf{H}_2CH_3)_A$; 1·18, m, $(C\mathbf{H}_2CH_3)_B$; 4·51, m, CH; 7·05–7·63, m, aromatic. ^{13}C n.m.r. δ ($CDCl_3$) 9·50, 9·53, 18·4, 18·8, 28·1, 28·5, 71·3, 71·4, 75·2 (d, J 108 Hz), 124·3 (d, J 93·4 Hz), 125·5, 125·8, 127·1, 127·2, 127·5, 127·8, 127·9, 128·07, 128·13, 128·3, 128·7 (d, J 12·8 Hz), 129·15, 129·23, 129·4, 129·5, 131·9, 132·0, 132·2, 132·9, 133·2 (d, J 10·2 Hz), 133·5, 133·6, 136·1, 136·2, 136·9, 137·1, 138·6, 141·2, 166·1 (d, J 13·7 Hz), 166·3 (d, J 15·2 Hz), 171·00, 171·05, 192·3 (d, J 3·7 Hz), 192·7 (d, J 3·8 Hz). ^{13}P n.m.r. δ ($CDCl_3$) 17·78.

A solution of the phosphoranes (4b) (50 mg, 0·08 mmol) in tetrahydrofuran was treated with an excess of diazomethane. Evaporation under reduced pressure and crystallization from ethyl acetate/light petroleum gave *methyl 2′-[2-(1-methylpropoxycarbonyl)-1-oxo-2-*

(triphenylphosphoranylidene)ethyl]-1,1′-biphenyl-2-carboxylate (5b) (39·0 mg, 76%), m.p. 123–124° (Found: C, 76·0; H, 5·7. $C_{39}H_{35}O_5P$ requires C, 76·2; H, 5·7%). ν_{max} 1720, 1660 cm^{-1}. ^1H n.m.r. δ ($CDCl_3$) 0·52, t, J 7·5 Hz, $CH_2\mathbf{CH_3}$; 0·56, d, J 6·3 Hz, $CH\mathbf{CH_3}$; 0·90, m, $\mathbf{CH_2}CH_3$; 3·42, s, OCH_3; 4·48, sextet, J 6·3 Hz, $\mathbf{CH}CH_3$; 7·13–7·95, m. ^{13}C n.m.r. δ ($CDCl_3$) 9·7, 18·7, 28·3, 51·6, 69·9, 72·2 (d, J 109 Hz), 126·1, 126·3 (d, J 93·2 Hz), 126·4, 126·5, 126·6, 127·4, 128·3 (d, J 12·5 Hz), 128·7, 129·2, 130·0, 130·5, 131·0, 131·5 (d, J 2·9 Hz), 131·9, 133·4 (d, J 9·8 Hz), 142·7, 166·5 (d, J 14·7 Hz), 167·9, 192·8 (d, J 5·7 Hz). ^{31}P n.m.r. δ ($CDCl_3$) 17·84.

Crystallography

General

Intensity data were collected at 160 K on a Nicolet R3m four-circle diffractometer, graphite-monochromatized Mo Kα radiation (λ 0·7107 Å) being used.

The structures were solved by direct methods with the SHELXTL (version 4.1) package.[8] Tabulations of structure factors, hydrogen atom coordinates and anisotropic thermal parameters have been deposited with the Australian Journal of Chemistry, 314 Albert Street, East Melbourne, Vic. 3002.

Data for (4a)

$C_{36}H_{29}O_5P$, M 572·6, crystal dimensions 0·5 by 0·6 by 0·06 mm, monoclinic, a 9·648(8), b 22·912(7), c 13·244(7) Å, β 96·89(6)°, V 2906(4) Å^3, space group $P2_1/n$, $Z = 4$, $F(000)$ 1200. Cell parameters were determined by least-squares refinement of 24 accurately centred reflections in the range $4·5° < 2\theta < 25°$. By using 2·1° ω-scans at scan rate of 4·88° min^{-1}, 3817 unique reflections were collected in the range of $4° < 2\theta < 45°$, and 1529 of these having $I > 3\sigma(I)$ were used in the structural analysis, R 0·069, R_w 0·036. Non-hydrogen atoms P, O(1), O(2), O(3), O(4), O(5), C(1), C(2), C(3), C(4), C(5), C(6) were refined anisotropically; the remaining non-hydrogen atoms were refined isotropically. All hydrogen atoms were inserted at calculated positions except for the hydrogen-bonded H which was located from a difference-Fourier map, inserted at that position and not further refined. Data were corrected for Lorentz and polarization effects but not for absorption.

Data for (5a)

$C_{37}H_{31}O_5P.CHCl_3$, M 586·6, crystal dimensions 0·48 by 0·38 by 0·24 mm, triclinic, a 10·612(2), b 13·615(3), c 14·189(4) Å, α 113·29(2), β 99·66(2), γ 107·75(2)°, V 1693·1(8) Å^3, space group $P\bar{1}$, $Z = 2$, $F(000)$ 616·0. Cell parameters were determined by least-squares refinement of 25 accurately centred reflections in the range $5° < 2\theta < 35°$. By using 1·6° ω-scans at a scan rate of 6·00° min^{-1}, 5321 unique reflections were collected in the range of $4° < 2\theta < 48°$, and 3785 of these having $I > 3\sigma(I)$ were used in the structural analysis, R 0·039, R_w 0·040. Data were corrected for Lorentz and polarization effects but not for absorption.

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[8] Sheldrick, G. M., SHELXTL User Manual+Package, Revision 4.1, Nicolet XRD Corporation, Madison, Wisconson, 1984.