Structure of the Product obtained from the Reaction of an αα′-Dibromophosphane Oxide with 1,5-Diazabicyclo[4.3.0]non-5-ene and Other Bases[1]

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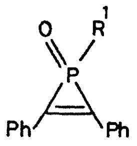
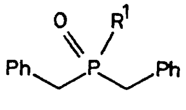
Summary The compound previously assigned a triphenylphosphiren oxide structure, as well as other base-induced rearrangement products of bis-(α-bromobenzyl)phenylphosphane oxide, are shown to be (*E*)-1,2-diphenylvinyl(phenyl)phosphinic acid derivatives.



(1)



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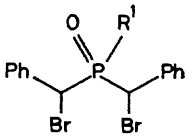
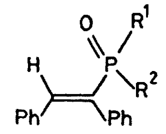
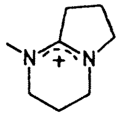
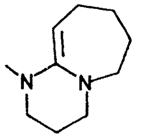


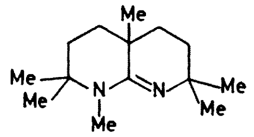
(3)

a; R^1 = OMe
b; R^1 = Ph



(4)

	R^1	R^2
a	OH	OH
b	OMe	OMe
c	Ph	OH
d	Ph	OMe
e	Ph	OBu^t
f	Ph	 Br$^-$
g	Ph	
h	Ph	Ph



(5)

Recently, the search for interesting heterocyclopropenes, *e.g.* oxirens,[2] thiirens,[3] selenirens,[3] and silirens,[4] has met with remarkable success. One such system, *viz.* 1-methoxy-2,3-diphenylphosphiren oxide (**1a**), has been invoked as one possible intermediate in the formation of the (*E*)-diphenylvinylphosphonate (**4b**) and the corresponding (*Z*)-diastereoisomer from (**3a**) and sodium methoxide in methanol.[5] The isolation of triphenylphosphiren oxide (**1b**) itself ('one member of a new class of potentially aromatic phosphacyclopropenes'[6]) has been reported. Thus, addition of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) to a solution of bis-(α-bromobenzyl)phenylphosphane oxide (**3b**) in benzene afforded, besides DBN hydrobromide, a light yellow oil which also apparently contained DBN hydrobromide. Structure (**1b**) was assigned to this oil on the basis of its mass spectrum (M^+, *m/e* 302; diphenylacetylene, *m/e* 178), its conversion on pyrolysis at 120 °C and 10^{-5}—10^{-6} Torr into diphenylacetylene, and the formation of the (*E*)-1,2-diphenylvinyl(phenyl)phosphinic acid (**4c**) (m.p. 160—163 °C) on addition of aqueous sodium hydroxide. Assignment of the (*E*)-configuration to (**4c**) was based on its pyrolysis which afforded (*Z*)- and (*E*)-stilbene (3 : 1).[6] However, proof of the symmetry of what was assumed to be (**1b**) was lacking. Furthermore, it was not possible to obtain a product free from DBN hydrobromide. This is not surprising since we now find that the compound which had been assigned the triphenylphosphiren oxide structure (**1b**) is actually the (*E*)-1,2-diphenylvinylphosphinic acid derivative (**4f**) as are the other products (**4d**), (**4e**), and (**4g**) obtained from reactions of the dibromophosphane oxide (**3b**) and strong bases.

Dibenzylphenylphosphane oxide (**2b**) was brominated by bromine in tetrachloromethane at 140—150 °C in sealed tubes affording a 50% yield of the dibromophosphane oxide (**3b**) as a mixture of diastereoisomers and 6% of the monobromophosphane oxide, after chromatography (SiO_2; ether–pentane, 3 : 1). In order to facilitate the interpretation of the n.m.r. spectra, $[^2H_5]$-(**3b**), fully deuteriated in the *P*-phenyl group, was prepared similarly.

Treatment of (**3b**) in benzene with 2 mol. equiv. of DBN produced a light yellow oil in agreement with the earlier findings.[6] Addition of water to this oil afforded the phosphinic acid (**4c**) (m.p. 145—146 °C) the (*E*)-configuration of which we have now confirmed by ^{1}H and ^{13}C n.m.r. spectroscopy (*vide infra*). However, repeated attempts to detect diphenylacetylene (by g.l.c.) on pyrolysis at 120 °C and 10^{-5} Torr failed. The i.r. spectrum of the product from (**3b**) and DBN did not exhibit the reported P=O frequency at 1265 cm^{-1} (bands were observed at 1305, 1235, 1208, and 1173 cm^{-1}) nor did the mass spectrum show a molecular ion at *m/e* 302. The mass spectrum of the product obtained from (**3b**) and $[7,7-^2H_2]$DBN showed that the ions could be separated into two types: one type containing DBN {*m/e* 427 [1%, (**4f**) − Br], 426 (3%, −HBr), 425 (2%, −Br, −2H), 424 (5%, −Br, −3H), 349 (4%, −HBr, −C_6H_5), 347 (3%, −Br, −3H, −C_6H_5), 307 (8%), 306 (38), 305 (34), and 304 (10%)} and the other without DBN [*m/e* 622 (4%), 444 (5), 367 (2), 321 (16), 303 (18), and 178 (100)]. The ion of *m/e* 622 and the other DBN-free ions except the ion of *m/e* 178 arise from the anhydride of the phosphinic acid (**4c**) apparently resulting from traces of moisture. The

DBN-containing ions are only compatible with a structure consisting of parts from both reactants (**3b**) and DBN. This result is corroborated by the n.m.r. spectra: besides the phenyl multiplet and the supposed DBN signals, the ^{1}H n.m.r. spectrum of the product from (**3b**) and DBN exhibited a sharp 1-proton doublet at δ 7·80 coupled to the phosphorus with J_{HP} 24·2 Hz. This doublet, which was observed for the first time when C_6D_6 was used as the solvent or [$^{2}H_5$]-(**3b**) as the starting material, as well as the ^{13}C n.m.r. spectra, are characteristic of an (*E*)-1,2-diphenylvinyl(phenyl)phosphinic acid derivative as shown by comparison with the n.m.r. spectra of the 1,2-diphenylvinylphosphorus compounds (**4a**),[7] (**4b**),† and (**4h**)[8] of known (*E*)-configuration (Table). Both ^{1}H and ^{13}C n.m.r. spectra definitively rule out the triphenyl-phosphiren oxide structure (**1b**). Moreover, P-coupling of several DBN ^{13}C signals showed that the DBN unit was actually attached to the phosphorus atom, probably *via* N-5.

TABLE. N.m.r. data for the (*E*)-1,2-diphenylvinyl-phosphorus compounds (**4a**—**4h**) in $CDCl_3$ unless otherwise stated. Phosphorus coupling constants are given in brackets [Hz].

	^{1}H n.m.r. δ_H		^{13}C n.m.r. δ_C/p.p.m.			
Compound	PhC*H*=	R^2	Ph*C*H=	=*C*(Ph)P	Quat. phenyl-C attached to vinyl group	R^2
(**4a**)[a]	7·50 [23·4]	9·7	141·4 [10·3]	135·7 [178·7]	136·3 [22·1], 137·5 [8·8]	
(**4b**)	7·65 [24·7]	3·76 [11·0]	144·4 [11·0]	129·9 [180·2]	134·5 [22·8], 135·4 [8·1]	52·7 [5·9]
(**4c**)	7·60 [22·1]	11·8	141·3 [10·3]	b	134·9 [19·1], 135·3 [8·8]	
(**4d**)[c]	8·06 [21·0]	3·48 [10·9]	143·0 [11·0]	b	134·7 [19·1], 135·5 [8·8]	51·3 [5·9]
(**4e**)	7·58 [22]	1·51 (s)	140·7 [11·0]	b	135·2 [19·1], 136·1 [8·8]	83·6 [8·1] 30·9 [3·7]
(**4f**)[d]	7·80 [24·2]	1·7—2·2 (m), 2·8—3·1 (m), 3·2—4·0 (m)	147·0 [13·5]	b	133·3 [18·4], 134·3 [10·3]	169·1 [7·4] (C-6), 55·6, 52·0, 44·5, 34·6 [4] (C-7), 19·1, 18·8
(**4g**)[e]	8·20 [21·6]	1·90 (dt, *J* 6·4, 5·4, 2 × H-5), 5·35 (dt, *J* 6·4, [1·2], H-6), 1·1—1·7 (m), 2·4—3·3 (m)	145·6 [9·6]	b	136·0 [18·4], 137·5 [8·8]	149·2 [4·4] (C-7), 96·5 [2·9] (C-6), 54·8, 48·6 [10], 42·0 [5], 31·3, 28·9, 26·2 [4.4], 24·1 [5]
(**4h**)			143·1 [9·6]	b	134·9 [17·6], 135·6 [8·8]	

[a] In $(CD_3)_2SO$ for ^{1}H and CD_3OD for ^{13}C. [b] Unequivocal assignment not possible. [c] In C_6D_6 for ^{1}H and $CDCl_3$ for ^{13}C. [d] In C_6D_6. [e] In CD_2Cl_2.

Addition of a slight excess of methanol to a solution of the product from (**3b**) and DBN slowly produced DBN hydrobromide and the methyl phosphinate (**4d**) quantitatively (as monitored by ^{1}H n.m.r. spectroscopy). Workup yielded 79% of (**4d**) as a colourless oil after distillation at 10^{-5} Torr, bath temperature 120—140 °C. Compound (**4d**) was also obtained when (**3b**) in dry tetrahydrofuran (THF) was treated with sodium methoxide (80% yield after chromatography and distillation).

The mass spectra and the agreement between the n.m.r. data of the product from (**3b**) and DBN and the data for the other (*E*)-1,2-diphenylvinyl phosphorus compounds (**4**) as well as the products formed with water or methanol are most easily interpreted in terms of the structure (**4f**). The ionic nature of (**4f**) is corroborated by the fact that it was much less soluble in benzene than all the other compounds studied.

In contrast to the reaction with DBN, that with 3 mol. equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and (**3b**) furnished 2 mol. equiv. of DBU hydrobromide and a product soluble in benzene. Besides the vinyl doublet at δ 8·20 the ^{1}H n.m.r. spectrum of this product showed a 1-proton triplet (*J* 6·4 Hz) at δ 5·35 which was further split by P-coupling (J_{HP} 1·2 Hz) (Table). The carbon to which this vinyl proton was attached absorbed at 96·5 p.p.m. in the ^{13}C n.m.r. spectrum and was also coupled to phosphorus (J_{CP} 2·9 Hz). Again, with methanol (**4d**) was slowly formed. We assign structure (**4g**) to the product from (**3b**) and DBU.

Surprisingly, (**3b**) and the non-nucleophilic bicyclic amidine (**5**) which is more basic than DBU[9] did not react in C_6D_6 or in CD_2Cl_2 below 70 °C. Heating above 70 °C slowly induced decomposition into uncharacterized products. The same behaviour was observed when ethyldi-isopropylamine or tris-(2,2-dimethylpropyl)amine[10] were used as base. As expected, reaction of (**3b**) and potassium t-butoxide in THF furnished the rearranged product (**4e**) (71%, m.p. 106—108 °C).‡ As in the case of (**3a**),[5] there

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† Prepared from (**4a**) by treatment with phosphorus(V) chloride followed by methanol and triethylamine in benzene, m.p. 70—71 °C.

‡ Compounds (**4b**)—(**4e**), and (**4h**) were characterized by elemental analysis, and mass and i.r. spectroscopy in addition to their n.m.r. spectra.

are several ways to rationalize the base-induced, Favorskii-like rearrangement of the dibromophosphane oxide (**3b**) to the vinylphosphinic acid derivatives (**4**). The true triphenyl-phosphiren oxide (**1b**) may be involved in this rearrangement but its existence has yet to be proved.

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