Phosphorus Heterocycles. Part I. A Conjugated Cyclic Methylenephosphorane

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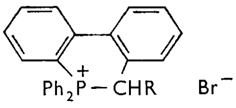
The cyclic quaternary phosphonium salt 9,10-dihydro-9,9-diphenyl-9-phosphoniaphenanthrene bromide reacts with aqueous sodium hydroxide to give the corresponding cyclic methylenephosphorane as an incompletely characterised orange solid, the relative stability towards hydrolysis of which compared with its acyclic analogue, benzylidenetriphenylphosphorane, suggests some aromatic character in the phosphorus-containing ring.

Most methylenephosphoranes are readily hydrolysed and cannot be prepared in an aqueous medium, but some are considerably stabilised by resonance beyond that represented by the general formulation (Ia $\leftrightarrow$ Ib).

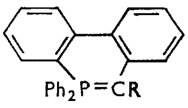
Such reduced reactivity is usually associated with delocalisation of the negative charge of the dipolar structure (Ib),[1] but it appeared that stabilisation might also result from inclusion of the formally double phosphorus–carbon bond of the covalent structure (Ia) in a completely conjugated six-membered ring, if this led to aromaticity in this ring. We have explored this possibility by comparing the actions of aqueous alkali upon 9,10-dihydro-9,9-diphenyl-9-phosphoniaphenanthrene bromide (II; R = H) and upon benzyltriphenylphosphonium chloride, and have found a difference in hydrolytic stability which we believe to indicate some aromatic character in the phosphorus-containing ring of the cyclic methylenephosphorane (III; R = H).

2-Bromo-2′-carboxybiphenyl was reduced by lithium aluminium hydride to 2-bromo-2′-hydroxymethylbiphenyl, which was converted by hydrogen bromide into 2-bromo-2′-bromomethylbiphenyl and thence, by solvolysis in methanol into 2-bromo-2′-methoxymethylbiphenyl. The Grignard reagent from this bromo-ether reacted with diphenylphosphinous chloride to give 2-diphenylphosphino-2′-methoxymethylbiphenyl (IV; R = H), a similar reaction sequence starting with *o*-bromobenzyl methyl ether having been carried out previously to establish reaction conditions. The phosphine (IV; R = H) cyclised quantitatively to the quaternary phosphonium bromide (II; R = H) when heated with hydrogen bromide in acetic acid.[2]

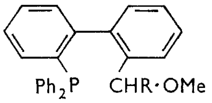
$$\text{(Ia)}\quad R_3P=CR_2 \longleftrightarrow R_3\overset{+}{P}-\overset{-}{C}R_2\quad\text{(Ib)}$$



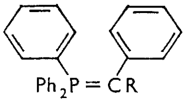
(II)



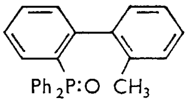
(III)



(IV)



(V)



(VI)

Addition of a cold aqueous solution of benzyltriphenylphosphonium chloride to cold aqueous sodium hydroxide gave only the most transient orange colour of benzylidenetriphenylphosphorane (V; R = H), changing immediately to a white suspension of hydrolysis products. Similar treatment of the cyclic quaternary phosphonium bromide gave a bright orange precipitate of the cyclic methylenephosphorane (III; R = H) which retained its colour for several hours. Although satisfactory analytical figures were not obtained, the ultraviolet spectrum was investigated and is shown in the Figure together with those of the cyclic phosphonium bromide, of 2-diphenylphosphinyl-2′-methylbiphenyl (VI), and of diphenylmethylenetriphenylphosphorane

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[1] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, 1957, **22**, 41; L. Horner and H. Oediger, *Chem. Ber.*, 1958, **91**, 437; L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.*, 1947, **69**, 723; F. Ramirez and S. Levy, *ibid.*, 1957, **79**, 67.

[2] M. H. Beeby and F. G. Mann, *J. Chem. Soc.*, 1951, 411; F. G. Mann and I. T. Millar, *ibid.*, 1951, 2205.

(V; R = Ph). The phosphine oxide (VI), the expected hydrolysis product of the cyclic methylenephosphorane, was formed after the appearance of a transient orange colour, when a solution of the cyclic phosphonium salt was added to aqueous sodium hydroxide at 100°, or when the moist cyclic methylenephosphorane was dissolved in acetone. No evidence could be found for Wittig reactions when benzaldehyde or *p*-nitrobenzaldehyde were added to ether solutions of the cyclic methylenephosphorane: a crystalline solid obtained from the experiment with benzaldehyde was found to be the hemibenzoate of the phosphine oxide (VI).

Cyclic methylenephosphoranes may be conveniently named by an extension of the Stelzner system,[3] using the prefix phospha(v) to indicate quinquevalent phosphorus, leading to 9,9-diphenyl-9-phospha(v)phenanthrene for our compound (III; R = H). Two phospha(v)naphthalenes [4] and a phospha(v)benzene [5] have been reported by Märkl who has found them also to be relatively resistant to hydrolysis and not to participate in Wittig reactions.

Although benzylidenetriphenylphosphorane (V; R = H) is very rapidly hydrolysed, diphenylmethylenetriphenylphosphorane (V; R = Ph) can be prepared in an aqueous medium and has resistance to hydrolysis similar to that of the cyclic methylenephosphorane (III; R = H). In view of this stabilising effect of an α-phenyl group, the preparation of 9,10-dihydro-9,9,10-triphenyl-9-phosphoniaphenanthrene bromide (II; R = Ph) was attempted since the corresponding cyclic methylenephosphorane (III; R = Ph) might well be sufficiently unreactive to be obtained pure. Treatment of 2,2′-dibromobiphenyl with one equivalent of butyl-lithium and then with benzaldehyde gave 2-bromo-2′-(α-hydroxybenzyl)biphenyl, which was converted by successive treatment with hydrogen bromide and methanol through 2-bromo-2′-(α-bromobenzyl)biphenyl into 2-bromo-2′-(α-methoxybenzyl)biphenyl. Attempts to convert this into 2-diphenylphosphino-2′-(α-methoxybenzyl)biphenyl (IV; R = Ph) failed: both the organolithium compound, formed from the bromo-ether by treatment with butyl-lithium, and the Grignard reagent, prepared under forcing conditions, underwent cyclisation to 9-phenylfluorene with displacement of the methoxyl group.

EXPERIMENTAL

2-*Bromo*-2′-*hydroxymethylbiphenyl*.—2-Bromo-2′-carboxybiphenyl [6] (25 g.) in ether (480 ml.) was added dropwise to a stirred refluxing solution of lithium aluminium hydride (5·6 g.) in ether (360 ml.). After 3 hr., wet ether was added, followed by 2N-sulphuric acid. The ether layer was separated, washed with 2N-sodium carbonate, and water, and dried. Evaporation of the solvent, and recrystallisation from light petroleum (b. p. 60—80°) gave the *biphenyl* (17·5 g., 74%), m. p. 83—83·5° (Found: C, 59·3; H, 4·4. $C_{13}H_{11}BrO$ requires C, 59·3; H, 4·2%).

2-*Bromo*-2′-*bromomethylbiphenyl*.— Hydrogen bromide was passed into 2-bromo-2′-hydroxymethylbiphenyl (30 g.) in benzene (400 ml.) for 3½ hr. The water which had formed was separated, the benzene was removed under reduced pressure, and the residue was recrystallised from light petroleum (b. p. 40—60°) giving the *biphenyl* (34·5 g., 93%), m. p. 55—57° (Found: C, 47·9; H, 3·35. $C_{13}H_{10}Br_2$ requires C, 47·7; H, 3·4%).

2-*Bromo*-2′-*methoxymethylbiphenyl*.—A solution of 2-bromo-2′-bromomethylbiphenyl (29·9 g.) in methanol (300 ml.) was heated under reflux for 24 hr. Removal of the solvent yielded a crystalline residue (25·2 g.) which was distilled to give the *biphenyl* (19·9 g., 78%), b. p. 140—150°/2 mm., m. p. 40—42° (Found: C, 60·7, 60·4; H, 4·6, 4·9. $C_{14}H_{13}BrO$ requires C, 60·6; H, 4·7%).

2-*Diphenylphosphino*-2′-*methoxymethylbiphenyl* (IV; R = H).—Diphenylphosphinous chloride (5·9 g.) in ether (50 ml.) was added to the Grignard reagent [prepared by the entrainment method [7] from 2-bromo-2′-methoxymethylbiphenyl (5·5 g.), ethyl bromide (0·7 g.), and activated [8] magnesium turnings (0·8 g.) in ether (100 ml.)] under nitrogen, and the mixture was boiled for 2½ hr. Dilute hydrochloric acid was added, the layers were separated, and the aqueous layer was extracted with ether. The combined ether layer and extracts were dried ($MgSO_4$), the ether was removed, and the more volatile part (probably largely ethyldiphenylphosphine) of the residue was distilled off at temperatures up to 140°/0·01 mm. The undistilled material was recrystallised three times from ethanol to give the *biphenyl* (2·8 g., 35%), m. p. 104·5—105·5° (Found: C, 82·1; H, 6·6; P, 8·0. $C_{26}H_{23}OP$ requires C, 81·7; H, 6·0; P, 8·1%).

o-(*Diphenylphosphino*)*methoxymethylbenzene*.—An experiment as above, but using *o*-bromobenzyl methyl ether (4·0 g.), yielded after distillation of the ethyldiphenylphosphine, a fraction (1·6 g.), b. p. 160—180°/0·35 mm. which solidified. Recrystallisation from ethanol yielded the *phosphino-compound*, m. p. 92·5—93·5° (Found: C, 78·2; H, 6·9; P, 10·4. $C_{20}H_{19}OP$ requires C, 78·4; H, 6·2; P, 10·1%).

9,10-*Dihydro*-9,9-*diphenyl*-9-*phosphoniaphenanthrene Bromide* (II; R = H).—Hydrogen bromide was passed into a boiling solution of 2-diphenylphosphino-2′-methoxymethylbiphenyl (2·0 g.) in glacial acetic acid (20 ml.) for 3 hr. The solvent was removed under reduced pressure yielding the *bromide* (2·2 g., 97%), m. p. 335—337° after two recrystallisations from acetic acid and one from ethanol–ethyl acetate (Found: C, 69·4; H, 4·8. $C_{25}H_{20}BrP$ requires C, 69·6; H, 4·6%).

Reaction of 9,10-*Dihydro*-9,9-*diphenyl*-9-*phosphoniaphenanthrene Bromide with Alkali*.—No reaction was apparent on adding aqueous ammonia or sodium carbonate to aqueous solutions of the cyclic phosphonium salt, but addition of 2N-sodium hydroxide produced an immediate orange precipitate.

A solution of the cyclic phosphonium salt (0·50 g.) in water (50 ml.) was cooled in ice and added to a cold solution of sodium hydroxide (5·0 g.) in water (25 ml.). Crude 9,9-*diphenyl*-9-*phospha*(v)*phenanthrene* (III; R = H) was precipitated as a bright orange solid which was filtered off, washed with water, and dried in a vacuum without ap-

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[3] " Handbook for Chemical Society Authors," 1960, p. 102.

[4] G. Märkl, *Angew. Chem.*, 1963, **75**, 168.

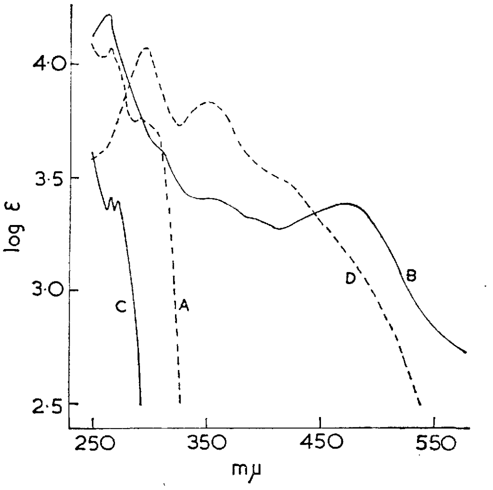
[5] G. Märkl, *Angew. Chem.*, 1963, **75**, 669.

[6] H. Gilman and R. D. Gorsich, *J. Amer. Chem. Soc.*, 1956, **78**, 2217.

[7] F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, 1947, 1634.

[8] F. C. Whitmore and D. E. Badertscher, *J. Amer. Chem. Soc.*, 1933, **55**, 1559.

parent change during several hours. The colour faded on prolonged standing in daylight, and more slowly in the dark. In a similar experiment at 100°, the orange colour of the cyclic methylenephosphorane disappeared before mixing was complete, and after cooling, extraction with benzene, and evaporation of the extract, there was obtained *2-diphenylphosphinyl-2′-methylbiphenyl* (VI), m. p. 154—156°, from light petroleum (b. p. 100—120°) (Found: C, 81·4; H, 5·9; P, 8·4. $C_{25}H_{21}OP$ requires C, 81·5; H, 5·7; P, 8·4%): the same product was also obtained when the moist cyclic methylenephosphorane was dissolved in acetone. When the cyclic methylenephosphorane, prepared at 0—10°, was extracted with ether, and benzaldehyde was added, there was obtained after slow evaporation, trituration of the resulting solid with dilute aqueous ammonia, and recrystallisation from aqueous alcohol and from light petroleum (b. p. 100—120°) *2-diphenylphosphinyl-2′-methylbiphenyl hemibenzoate*, m. p. 138—139° (Found: C, 79·9; H, 5·7; P, 7·2. $C_{57}H_{48}O_4P_2$ requires C, 79·6; H, 5·6; P, 7·2%) identical (m. p. and infrared spectrum) with a specimen prepared from the phosphine oxide (VI) and benzoic acid.



Ultraviolet spectra. *A*, 9,10-Dihydro-9,9-diphenyl-9-phosphoniaphenanthrene bromide (II; R = H) in ethanol; *B*, 9,9-diphenyl-9-phospha(v)phenanthrene (III; R = H); *C*, 2-diphenylphosphinyl-2′-methylbiphenyl (VI) in hexane; *D*, diphenylmethylenetriphenylphosphorane (V; R = Ph)

The ultraviolet spectrum of the cyclic methylenephosphorane was determined using a solution obtained by shaking the finely powdered cyclic phosphonium salt with 0·1M-potassium t-butoxide in 10% t-butyl alcohol–90% hexane. It is shown in the Figure for wavelengths greater than 250 mμ below which the solvent was opaque. The true values of the extinction coefficient may be somewhat higher than those observed because of slight decomposition in the dilute (10^{-4}M) solutions used, although the measurements were completed within 1 hr. with little or no apparent change in the solution. An attempt to obtain the spectrum of benzylidenetriphenylphosphorane (V; R = H) by the same technique was unsuccessful as the initial orange colour faded within 5 min. (providing another example of the higher reactivity of the acyclic methylenephosphorane) but the spectrum of diphenylmethylenetriphenylphosphorane (V; R = Ph) was similarly determined and is also shown in the Figure.

2-Bromo-2′-(α-hydroxybenzyl)biphenyl.—An ether solution of n-butyl-lithium (42 ml., 0·92M) was added with stirring to 2,2′-dibromobiphenyl (12·0 g.) in ether (200 ml.) under nitrogen at −30°. After 15 min., benzaldehyde (4·4 g.) in ether (40 ml.) was added, and stirring was continued until the temperature reached 10°. Water was added, and the ether layer was separated, dried ($MgSO_4$) and evaporated. The residue was dissolved in benzene and separated by chromatography on alumina into 2,2′-dibromobiphenyl eluted with benzene, *2-bromo-2′-(α-hydroxybenzyl)biphenyl* (9·5 g., 73%) eluted with ethyl acetate, and 2,2′-di-(α-hydroxybenzyl)biphenyl (1·0 g., 7%) eluted with ethanol and having m. p. 196—198° (lit.,[9] 193·5—194·5°) after two recrystallisations from ethanol (Found: C, 85·2; H, 6 ·1. Calc. for $C_{26}H_{22}O_2$: C, 85·3; H, 6·0%). 2-Bromo-2′-(α-hydroxybenzyl)biphenyl was obtained in two forms: of m. p. 90—90·5° from light petroleum (b. p. 60—80°) (Found: C, 67·7; H, 4·3. $C_{19}H_{15}BrO$ requires C, 67·3; H, 4·4%), and of m. p. 126·5—127·5° (undepressed by admixture with the lower-melting form) from ethanol–water (Found: C, 67·0; H, 4·7%).

2-Bromo-2′-(α-bromobenzyl)biphenyl and 2-Bromo-2′-(α-methoxybenzyl)biphenyl.—Hydrogen bromide was passed through a solution of 2-bromo-2′-(α-hydroxybenzyl)biphenyl (7·2 g.) in benzene (500 ml.) until no more water was formed. The solvent was removed under reduced pressure and the residue was recrystallised twice from hexane giving *2-bromo-2′-(α-bromobenzyl)biphenyl*, m. p. 84—85° (Found: Br, 39·0. $C_{19}H_{14}Br_2$ requires Br, 39·8%). In another experiment, the residue after removal of the benzene was dissolved in methanol (300 ml.) and heated under reflux for 3 hr. Removal of the methanol afforded *2-bromo-2′-(α-methoxybenzyl)biphenyl* (6·2 g., 83%), m. p. 75—76° after recrystallisation from methanol (Found: C, 67·9; H, 4·9. $C_{20}H_{17}BrO$ requires C, 68·0; H, 4·9%).

Attempted Preparation of 2-Diphenylphosphino-2-(α-methoxybenzyl)biphenyl (IV; R = Ph).—An ether solution of n-butyl-lithium (2·7 ml., 1·15M) was added to 2-bromo-2′-(α-methoxybenzyl)biphenyl (1·0 g.) in ether (50 ml.) under nitrogen. After 12 hr., diphenylphosphinous chloride (0·75 g.) in ether was added and the mixture was heated under reflux for 1 hr. Water was added, the ether layer was separated, washed with 2N-sodium carbonate, and water, dried ($MgSO_4$), and evaporated giving 9-phenylfluorene (0·6 g.), m. p. 146—146·5° (lit.,[10] 145°), after recrystallisation from methanol (Found: C, 94·3; H, 6·3. Calc. for $C_{19}H_{14}$: C, 94·2; H, 5·8%). A similar experiment using the Grignard reagent (prepared by the entrainment method using ethylene dibromide in di-n-butyl ether) also yielded 9-phenylfluorene.

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