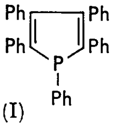
569. *Heats of Formation and Bond Energies. Part VII.* Pentaphenylphosphole, 9-Phenyl-9-phosphafluorene, and their Oxides.*

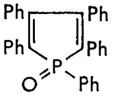
By A. F. Bedford, D. M. Heinekey, Ian T. Millar, and C. T. Mortimer.

The heats of combustion of crystalline pentaphenylphosphole and its oxide, and of 9-phenyl-9-phosphafluorene and its oxide to crystalline orthophosphoric acid, liquid water, and gaseous carbon dioxide have been measured as −4349·17 ± 3·4, −4308·26 ± 5·2, −2385·6 ± 2·0, and −2319·4 ± 6·0 kcal./mole, respectively. The derived heats of formation of the crystalline compounds are +93·7 ± 3·4, +52·8 ± 5·2, +44·9 ± 2·0, and −21·3 ± 6·0 kcal./mole, respectively. These results are used to estimate resonance energies. A new synthesis of 9-phenyl-9-phosphafluorene from 2,2′-dilithiobiphenyl and dichlorophenylphosphine in 45% yield is reported.

HETEROCYCLOPENTADIENES involving atoms other than oxygen, nitrogen, sulphur, selenium, or tellurium have only recently been prepared. Leavitt, Manuel, and Johnson [1] reported the synthesis of pentaphenylphosphole (I), in good yield, from 1,4-dilithio-1,2,3,4-tetraphenylbutadiene and dichlorophenylphosphine. Braye and Hübel [2] obtained pentaphenylphosphole oxide (II) by air oxidation of a solution of the phosphole.



(I)



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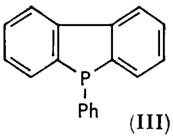
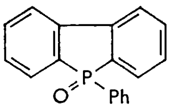


(III)



(IV)

Although not strictly a heterocyclic pentadiene, 9-phenyl-9-phosphafluorene (III) also has an unsaturated, five-membered ring which includes a phosphorus atom. This compound has been prepared by the thermal decomposition of pentaphenylphosphorane,[3,4] and in low yield by the reaction of triphenylphosphine with benzyne [5] or phenylsodium.[3] 9-Phenyl-9-phosphafluorene oxide (IV) has been obtained by cyclisation of 2-biphenylylphenylphosphinic acid [6] and, in very low yield, by reaction of 2,2′-dilithiobiphenyl with dichlorophenylphosphine and concurrent oxidation by air.[3] We find that the phosphafluorene can readily be prepared in fair yield by an extension of the general method previously described [7] for the synthesis of 9-arsa- and 9-stibia-fluorenes, by reaction of 2,2′-dilithiobiphenyl with dichlorophenylphosphine; and that the oxide is conveniently obtained in high yield by oxidation with hydrogen peroxide.

These preparations make the compounds (I—IV) readily available in quantities sufficient for heats of combustion to be measured, and these are reported in this paper. The interest in these experimental results lies in their use to estimate resonance energies. Molecular-orbital calculations, made by Brown,[8] indicate a reasonable conjugation energy for the phosphole and the phosphole oxide, on the assumption that they are planar. However, on the chemical evidence available, it has been concluded [2,9] that the phosphole behaves as a conjugated diene and possesses little or no aromatic character.

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* Part VI, preceding paper.

[1] Leavitt, Manuel, and Johnson, *J. Amer. Chem. Soc.*, 1959, **81**, 3163.

[2] Braye and Hübel, *Chem. and Ind.*, 1959, 1250.

[3] Wittig and Geissler, *Annalen*, 1953, **580**, 44.

[4] Razuvaev and Osanova, *Zur. obshchei Khim.*, 1956, **26**, 2531.

[5] Wittig and Benz, *Chem. Ber.*, 1959, **92**, 1999.

[6] Campbell and Way, *Proc. Chem. Soc.*, 1959, 231.

[7] Heinekey and Millar, *J.*, 1959, 3101.

[8] Brown, University College, Dublin, personal communication, 1961.

[9] Leavitt, Manuel, Johnson, Matternas, and Lehman, *J. Amer. Chem. Soc.*, 1960, **82**, 5099.

EXPERIMENTAL

Compounds.—Pentaphenylphosphole and its oxide were supplied by Dr. D. A. Brown of University College, Dublin. The phosphole had m. p. 254—255° (lit.,[2,9] 255—256°, 256—257°). The oxide had m. p. 283—284° (lit.,[2] 284—285°.)

9-Phenyl-9-phosphafluorene. 2,2′-Dibromobiphenyl (10 g.) in ether (150 ml.) was added during 2 hr. to a stirred suspension of lithium foil (1·5 g.) in ether (50 ml.) under nitrogen. After being stirred for a further 2 hr. the solution was decanted under nitrogen from the excess of lithium, and dichlorophenylphosphine (5·6 g., 1 mol.) in benzene (50 ml.) added during 20 min. After boiling under reflux for 1 hr. the mixture was cooled and hydrolysed with cold air-free water and the organic layer separated, dried (Na_2SO_4), and evaporated under nitrogen. Distillation in nitrogen gave biphenyl, b. p. 70°/0·05 mm. (0·3 g.), followed by the phosphafluorene, b. p. 152—156°/0·05 mm. (3·7 g., 45%), which after recrystallisation from ethanol had m. p. 94·5—95° (lit.,[3] m. p. 93—94°) (Found: C, 82·7; H, 5·3. Calc. for $C_{18}H_{13}P$: C, 83·05; H, 5·05%).

A sample with methyl iodide readily gave *9-methyl-9-phenyl-9-phosphoniafluorene iodide*, m. p. 204—205° [from ethanol–light petroleum (b. p. 60—80°)] (Found: C, 57·4; H, 4·15. $C_{19}H_{16}IP$ requires C, 57·0; H, 4·0%), $\lambda_{max.}$ (in 95% ethanol) ($\log_{10} \varepsilon$ in parentheses) 228 (4·69), 236 (4·70), 244 (4·61), 270 (3·89), 276 (3·89), $\lambda_{min.}$ 232 (4·68), 242 (4·60), 261 (3·84), and 273 mμ (3·87).

Leaving the phosphafluorene in acetone mixed with a slight excess of dilute aqueous hydrogen peroxide overnight gave, after removal of the solvents, a nearly quantitative yield of 9-phenyl-9-phosphafluorene 9-oxide, m. p. 163·5—164° (from aqueous ethanol) (lit.,[6] m. p. 167—168°) (Found: C, 78·7; H, 4·0. Calc. for $C_{18}H_{13}OP$: C, 78·25; H, 4·6%), $\lambda_{max.}$ (in 95% ethanol) 239 (4·64), 246 (4·63), 273 (3·75), 282 (3·77), 292 (3·67), $\lambda_{min.}$ 243 (4·56), 262 (3·62), 277 (3·70) and 288 mμ (3·54).

Combustion Calorimetry.—Combustions were made in a twin-value bomb (the Parr Instrument Co., Moline, Illinois, U.S.A.) which together with the subsidiary apparatus has been described previously.[10] The solid compounds were compressed into pellets. The bomb was charged with oxygen at an initial pressure of 30 atm. and with 1 ml. of water. Each sample was fired at 25°. All combustions were initiated by a platinum wire and cotton-thread fuse. This was sufficient to cause almost complete combustion of the phosphafluorene and its oxide, but with the phosphole and its oxide only partial burning resulted. The phosphole and its oxide were sealed in Melinex bags and for some combustions an extra fuse of benzoic acid was added. The crucible was covered with a platinum-wire gauze, to prevent the powdery compounds from being blown out before complete combustion.

Analysis.—After each combustion the bomb gases were analysed for carbon dioxide with an accuracy of ±0·02%. A part of the bomb-washings was titrated with 0·1N-sodium hydroxide, thymolphthalein being used as indicator, to give the total phosphorus acid and nitric acid. A second part was treated with acetic acid, sodium acetate, and mercuric chloride. In no case was mercurous chloride precipitated, showing the absence of phosphorous acids. A third part was analysed for orthophosphoric acid by the quinoline–phosphomolybdate method [11] to an accuracy of ±0·1%. A fourth part was boiled with nitric acid to convert condensed acids into the ortho-acid, and the total phosphoric acid found. In no case was any condensed phosphoric acid found. The quantity of phosphate recovered corresponded closely to the theoretical amount formed, as calculated from the recovery of carbon dioxide.

Units and Auxiliary Quantities.—The heats of combustion are given in units of the thermochemical calorie, 1 cal. = 4·180 abs. J. The energy equivalent of the calorimeter was determined by combustion of a sample of benzoic acid having $-\Delta U_b = 6\cdot3181 \pm 0\cdot0007$ cal./g. The heats evolved in the processes (*a* — *c*) of the preceding paper were taken as there, and also (*d*) the solution of crystalline phosphoric acid to give a 1·0N-solution, 2·9 kcal./mole,[12] and (*e*) the combustion of carbon (soot) to carbon dioxide, 8·11 kcal./g.[13]

Results.—The results of the combustions are given in Tables 1—4, in which the symbols have the same meanings as previously.[14]

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[10] Fletcher, Mortimer, and Springall, *J.*, 1959, 580.

[11] Wilson, *Analyst*, 1951, **76**, 55.

[12] National Bureau of Standards Circular 500, Washington, D.C., 1952.

[13] Coops, Kentie, and Dienske, *Rec. Trav. chim.*, 1947, **66**, 113.

[14] Bedford and Mortimer, *J.*, 1960, 1622.

Only those combustions of pentaphenylphosphole, 9-phenyl-9-phosphafluorene and 9-phenyl-9-phosphafluorene oxide for which values of CO_2 obs. : calc. were greater than 99·70% were accepted. Values which were less than 100·00% are interpreted as in the preceding paper. Since some combustions of each of these three compounds gave values of CO_2 obs. : calc. of 99·96%, or greater, it seems unlikely that the samples contained organic impurities.

For pentaphenylphosphole oxide the values of CO_2 obs. : calc. ranged from 99·24 to 99·54%. This compound was very powdery and difficult to pellet, and since carbon and traces of unburnt compound were found in the bomb after combustion, it was assumed that low recovery of carbon dioxide was due to incomplete combustion. It may be, however, that traces of organic impurity were present. As the correction due to low recovery was comparatively large in this case, the results for this compound are less reliable than for the others.

The mass of sample burnt in each experiment was calculated from the mass of carbon dioxide and carbon formed (uncertainty ±0·02), the cotton fuse, benzoic acid, and Melinex fuse being assumed to have been burnt completely. In each case the uncertainty associated with the ΔH_c^0 values is twice the standard deviation of the mean.

The ΔH_c^0 values refer to the reactions:

$$(C_6H_5)_5C_4P\text{ (cryst.)} + 41{\cdot}5O_2\text{ (g)} \longrightarrow H_3PO_4\text{ (cryst.)} + 34CO_2\text{ (g)} + 11H_2O\text{ (liq.)}$$

$$(C_6H_5)_5C_4PO\text{ (cryst.)} + 41O_2\text{ (g)} \longrightarrow H_3PO_4\text{ (cryst.)} + 34CO_2\text{ (g)} + 11H_2O\text{ (liq.)}$$

$$C_{12}H_8PC_6H_5\text{ (cryst.)} + 22{\cdot}5O_2\text{ (g)} \longrightarrow H_3PO_4\text{ (cryst.)} + 18CO_2\text{ (g)} + 5H_2O\text{ (liq.)}$$

$$C_{12}H_8P(O)C_6H_5\text{ (cryst.)} + 22O_2\text{ (g)} \longrightarrow H_3PO_4\text{ (cryst.)} + 18CO_2\text{ (g)} + 5H_2O\text{ (liq.)}$$

Using the ΔH_f^0 values: H_2O (liq.), −68·3174; CO_2 (g), −94·0518; and H_3PO_4 (cryst.), −306·2 kcal./mole,[12] we calculate the ΔH_f^0 (cryst.) values: pentaphenylphosphole,

TABLE 1.

Pentaphenylphosphole: *M*, 464·515.

Expt.	1	2	3	4
Wt.* sample (g.)	0·271150	0·263951	0·370087	0·239699
ΔR_c (ohm)	0·13394	0·13843	0·09436	0·12122
CO_2 obs. : calc. (%)	99·92	99·80	99·96	99·96
q_m (cal.)	418·24	321·84	313·90	—
q_b (cal.)	2414·24	2759·20	—	2610·46
q_i (cal.)	12·26	12·49	14·28	14·17
q_n (cal.)	—	0·37	1·30	—
q_p (cal.)	0·20	0·17	0·23	0·12
q_w (cal.)	1·05	1·02	1·43	0·93
E_c (cal./ohm)	6·7	6·9	4·5	6·3
$-\Delta U_c^0$ (kcal./mole)	4343·24	4345·67	4342·32	4347·58

$-\Delta U_c^0$ mean value = 4344·70 kcal./mole (standard deviation of mean ±1·20 kcal./mole). E_s = 40154·0 cal./ohm; $\bar{s}E = \pm 0{\cdot}03\%$; $\bar{s}\Delta U_c^0 = \pm 0{\cdot}03\%$; $\bar{s} = \pm 0{\cdot}04\%$; $\Delta n\boldsymbol{R}T = -4{\cdot}47$ kcal./mole; $-\Delta H_c^0$ = 4349·2 ± 3·4 kcal./mole.

* All weights *in vacuo*.

TABLE 2.

Pentaphenylphosphole oxide: *M*, 480·515.

Expt.	1	2	3	4	5
Wt. sample (g.)	0·201077	0·176596	0·231436	0·464578	0·466018
ΔR_c (ohm)	0·9453	0·11426	0·11463	0·10978	0·11095
CO_2 obs. : calc. (%)	99·27	99·54	99·47	99·24	99·48
Wt. carbon (g.)	0·00076	0·00016	0·00020	0·00078	0·00233
q_m (cal.)	310·33	286·36	291·37	270·73	315·67
q_b (cal.)	1693·96	2722·20	2243·54	—	—
q_i (cal.)	6·88	6·49	7·18	7·58	10·70
q_n (cal.)	6·22	—	—	1·02	—
$-q_c$ (cal.)	6·15	1·28	1·62	6·29	18·85
q_p (cal.)	0·13	0·11	0·14	0·28	0·28
q_w (cal.)	0·87	0·76	1·00	2·00	2·01
E_c (cal./ohm)	4·7	5·9	5·8	5·3	5·4
$-\Delta U_c^0$ (kcal./mole)	4308·96	4302·70	4303·79	4307·90	4297·09

$-\Delta U_c^0$ mean value = 4304·09 kcal./mole (standard deviation of mean ±2·10 kcal./mole). E_s = 40154·0 cal./ohm; $\bar{s}E = \pm 0{\cdot}03\%$; $\bar{s}\Delta U_c^0 = \pm 0{\cdot}05\%$; $\bar{s} = \pm 0{\cdot}06\%$; $\Delta n\boldsymbol{R}T = -4{\cdot}17$ kcal./mole; $-\Delta H_c^0$ = 4308·3 ± 5·2 kcal./mole.

TABLE 3.

9-Phenyl-9-phosphafluorene: *M*, 260·259.

Expt.	1	2	3	4	5
Wt. sample (g.) ...	0·387655	0·661688	0·659986	0·62646	0·53611
ΔR_c (ohm)	0·08906	0·15202	0·15152	0·14393	0·12318
CO_2 obs. : calc. (%)	99·92	100·00	99·96	99·99	100·00
q_i (cal.)	5·32	5·45	5·86	5·99	5·20
q_n (cal.)	—	—	—	—	—
q_p (cal.)	4·10	6·53	6·51	6·18	5·45
q_w (cal.)	1·43	2·71	2·70	2·43	2·09
E_c (cal./ohm)	4·9	8·2	8·2	7·9	6·8
$-U_c^0$ (kcal./ohm) ...	2383·3	2383·1	2382·2	2383·2	2382·9

$-\Delta U_c^0$ mean value = 2382·9 kcal./mole (standard deviation of mean ±0·22 kcal./mole). E_s = 39944·6 cal./ohm; $\bar{s}E = \pm 0{\cdot}04\%$; $\bar{s}\Delta U_c^0 = \pm 0{\cdot}01\%$; $\bar{s} = \pm 0{\cdot}04\%$. $\Delta n\boldsymbol{R}T = -2{\cdot}7$ kcal./mole; $-\Delta H_c^0 = 2385{\cdot}6 \pm 2{\cdot}0$ kcal./mole.

TABLE 4.

9-Phenyl-9-phosphafluorene oxide: *M*, 276·259.

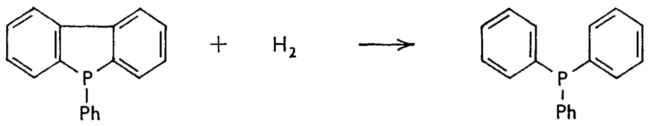
Expt.	1	2	3	4	5
Wt. sample (g.) ...	0·528020	0·512526	0·428142	0·468000	0·355328
ΔR_c (ohm)	0·11062	0·10770	0·08997	0·09786	0·07438
CO_2 obs. : calc. (%)	99·73	99·71	100·02	99·96	99·78
q_i (cal.)	5·59	5·39	5·12	5·16	4·89
q_n (cal.)	—	—	—	—	—
q_p (cal.)	5·06	4·94	4·18	4·52	3·56
q_w (cal.)	2·08	2·02	1·51	1·65	1·11
E_c (cal./ohm)	6·3	6·1	5·1	5·6	4·1
$-\Delta U_c^0$ (kcal./mole)	2318·6	2326·1	2316·9	2308·8	2314·6

$-\Delta U_c^0$ mean value = 2317·0 kcal./mole (standard deviation of mean ±2·8 kcal./mole). E_s = 40061·9 cal./ohm; $\bar{s}E = \pm 0{\cdot}04\%$; $\bar{s}\Delta U_c^0 = \pm 0{\cdot}12\%$; $\bar{s} = \pm 0{\cdot}13\%$; $\Delta n\boldsymbol{R}T = -2{\cdot}4$ kcal./mole; $-\Delta H_c^0 = 2319{\cdot}4 \pm 6{\cdot}0$ kcal./mole.

+93·7 ± 3·4; pentaphenylphosphole oxide, +52·8 ± 5·2; 9-phenyl-9-phosphafluorene, +44·9 ± 2·0; and 9-phenyl-9-phosphafluorene oxide, −21·3 ± 6·0 kcal./mole.

DISCUSSION

The heat of gas-phase hydrogenation, $\Delta H_{\text{hyd.}}$, of 9-phenyl-9-phosphafluorene to triphenylphosphine can be calculated from the heats of formation of the gaseous compounds. Two values are available for the heat of combustion, ΔH_c^0, of triphenylphosphine, —2463·3 ± 2·3 kcal./mole[14] and —2461·4 ± 3·6 kcal./mole, obtained from the data given by Birr.[15] This author actually gives the value —2458·4 ± 3·6 kcal./mole for the heat of combustion, but we have taken this to refer to ΔU_c^0, since no correction ($\Delta n\boldsymbol{R}T$ = —3·0 kcal./mole) appears to have been made for the disappearance of five moles of gas in the combustion reaction. The mean of these two ΔH_c^0 values leads to ΔH_f^0 (PPh_3, cryst.) = +53·3 ± 2·0 kcal./mole. The latent heat of sublimation of triphenylphosphine is estimated as 21·0 ± 0·5 kcal./mole, by adding 4·0 kcal./mole to the latent heat of vaporisation, which has been measured as 17·0 kcal./mole.[16] Hence we obtain ΔH_f^0 (PPh_3, g) = +74·3 ± 2·5 kcal./mole. The latent heat of sublimation of 9-phenyl-9-phosphafluorene has not been measured, but it is unlikely that it will differ from



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[15] Birr, *Z. anorg. Chem.*, 1960, **306**, 21.

[16] Forward, Bowden, and Jones, *J.*, 1949, S, 121.

that of triphenylphosphine by more than ±1·0 kcal./mole. Taking a value of 21·0 ± 1·5 kcal./mole, we obtain ΔH_f^0 (9-phenyl-9-phosphafluorene, g) = +65·9 ± 3·5 kcal./mole. From these data we calculate $\Delta H_{\text{hyd.}}$ = +8·4 ± 6·0 kcal./mole. In terms of bond energies we would expect the heat of hydrogenation to be given by $\Delta H_{\text{hyd.}} = E(\text{C–C}) + E(\text{H–H}) - 2E(\text{C–H})$, corresponding to the difference in the energies of the bonds broken and formed. Taking the values[17] E(C–C), 82·6; E(H–H), 104·2; and E(C–H), 98·7 kcal., we calculate $\Delta H_{\text{hyd.}}$ = —10·6 kcal./mole. We may interpret these values for the heat of hydrogenation to mean that 9-phenyl-9-phosphafluorene has a stabilisation or resonance energy of 19·0 kcal./mole. Unfortunately, the uncertainty associated with the heat of combustion of 9-phenyl-9-phosphafluorene oxide is too great to interpret the heat of hydrogenation to triphenylphosphine oxide in this way.

The bond dissociation energies, D(P=O), corresponding to the gas-phase dissociation of pentaphenylphosphole oxide to pentaphenylphosphole and an oxygen atom, and of 9-phenyl-9-phosphafluorene oxide to 9-phenyl-9-phosphafluorene and an oxygen atom, may be calculated from the thermochemical relations

$$D(\text{P=O}) = \Delta H_f^0[(C_6H_5)_5C_4P,\ g] + \Delta H_f^0(O,\ g) - \Delta H_f^0[(C_6H_5)_5C_4P(O),\ g],$$

and

$$D(\text{P=O}) = \Delta H_f^0(C_{12}H_8PC_6H_5,\ g) + \Delta H_f^0(O,\ g) - \Delta H_f^0[C_{12}H_8P(O)C_6H_5,\ g].$$

The latent heats of sublimation of none of these compounds has been reported, but it is unlikely that values for the phosphole and its oxide, or the phosphafluorene and its oxide will differ by more than ±1·0 kcal./mole. Taking the heats of formation of these compounds given above and the value $\Delta H_f^0(O,\ g)$ = 59·54 kcal./g.-atom,[17] we calculate the dissociation energies D(P=O) = 100·4 ± 9·5 kcal. for the phosphole oxide, and D(P=O) = 126·0 ± 9 kcal. for the phosphafluorene oxide. These bond dissociation energies may be compared with values of 128·4 ± 5·5 kcal.[14] for triphenylphosphine oxide, and 139·3 ± 3·0 kcal. for trimethylphosphine oxide.[18]

Although the uncertainties associated with these bond dissocation energies are large, there is a decrease in D(P=O) values along the series trimethylphosphine oxide, triphenylphosphine oxide, pentaphenylphosphole oxide. The position of the phosphafluorene oxide in this series is uncertain. This decrease may be due to the effect of conjugation involving the $3p_\pi$-orbital of the phosphorus atom. It appears that conjugation in pentaphenylphosphole, relative to its oxide, is greater than that in triphenylphosphine, relative to its oxide. Also, that this conjugation is greater than that in trimethylphosphine, relative to its oxide. In both of these last compounds the effects of conjugation are likely to be small. The difference, 39 ± 13 kcal., between the D(P=O) values for trimethylphosphine oxide and pentaphenylphosphole oxide may be taken as a measure of the conjugation energy of pentaphenylphosphole, relative to its oxide. Brown [8] has calculated the conjugation energy of the unsubstituted phosphole, C_4H_5P, to be about 1·5β. The conjugation energy of pentaphenylphosphole is likely to be larger than this. His calculations also show that the conjugation energy of the phosphole oxide is considerably less than that of the phosphole. Our results are in general agreement with Brown's predictions.

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[17] Cottrell, " The Strengths of Chemical Bonds," 2nd edn., Butterworths Scientific Publns., London, 1958.

[18] Claydon, Fowell, and Mortimer, *J.*, 1960, 3284.