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PHOSPHATRIPTYCENE

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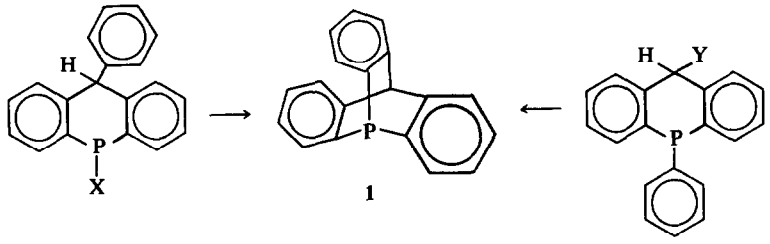
Abstract—Phosphatriptycene (**1**) is prepared by cyclizing 9-(*o*-chlorophenyl)-9,10-dihydrophosphaanthracene (**6**) with an excess of lithium diisopropylamide in ether. Its structure is confirmed by its ^{13}C-NMR spectrum. In nucleophilic reactions **1** is less reactive than triphenylphosphine. The nature of the bonding in quaternary phosphonium salts of **1** is discussed.

There has been considerable interest in the synthesis of triptycenes with heteroatoms in a bridgehead position[1] as the heteroatoms, due to the rigid environment, may be expected to show unusual bonding and chemical properties. Azaphosphatriptycene[2] and diphosphatriptycene[3] are known, but the simple phosphatriptycene (**1**) has not been reported so far.

In principle, the ring closure of a suitable dihydro-9-phosphaanthracene precursor to **1** might be accomplished starting from derivatives with a phenyl group attached to the meso-carbon atom or to phosphorus.



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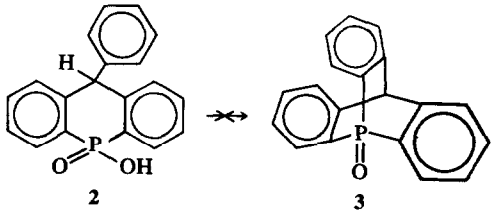
We explored the following three approaches:

Lynch[4] discovered, that *o*-phenylbenzylphosphonic acid could be cyclized to derivatives of the 9-phosphaphenanthrene ring system by heating to 350° *in vacuo*. We tried to cyclize the phosphinic acid (**2**) to phosphatriptycene oxide (**3**) by dehydration. Both the method of Lynch and heating with polyphosphoric acid were unsuccessful,[5] although arsatriptycene oxide was synthesized in this manner.[1]

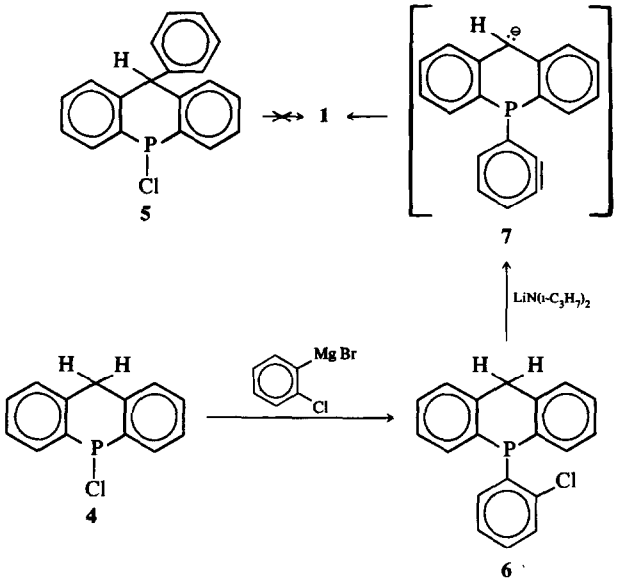


2 **3**

Doak and Freedman[6] found, that 2-dichlorophosphinodiphenylmethane was readily cyclized to 9 - chloro - 9,10 - dihydrophosphaanthracene (**4**). This synthesis was improved by de Koe and Bickelhaupt[7] by refluxing with anhydrous aluminium chloride in CS_2 and extended to the preparation of 9 - chloro - 10 - phenyl - 9,10 - dihydrophosphaanthracene (**5**).[8] Reacting **5** with anhydrous aluminum chloride or bromide we obtained a complex mixture probably containing a trace of **1** which, however, could not be isolated.

In the synthesis of azatriptycene[9] and azarsatriptycene[10] ring closure was achieved by intramolecular addition of nitrogen to a benzyne. In an analogous approach ring closure to **1** was achieved in 35% yield by cyclization of **6** with an excess of lithium diisopropylamide in ether, presumably by attack of the carbanionic centre in **7** on the benzyne. **6** was synthesized in 52% yield by reaction of **4** with *o*-chlorophenylmagnesium bromide.

Recrystallization of **1** from ethanol gave white crystals, m.p. 242–243°. The addition of triptycene depressed the m.p.; it is surprising that, contrary to the nitrogen[9] and arsenic analogue,[1] there seems to be no isomorphism with the parent compound. The UV spectrum of **1** is similar to that of arsatriptycene and triptycene itself, suggesting that there is no appreciable electronic interaction between the heteroatom and the aromatic rings. The IR spectrum of **1** closely resembles that of triptycene itself,



and from its lowest CH stretch vibration at 2950 cm^{-1} we conclude that **1** has a rigid structure.[11] The mass spectrum of **1** shows a molecular ion at $m/e = 272$ and doubly and triply charged ions of relatively high intensities.[2]

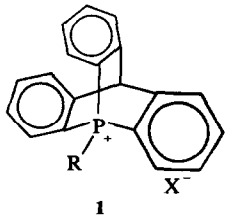
^{13}C-NMR is a very useful tool to corroborate the structure of **1**, because it has a threefold axis and consequently there are only seven different types of C atoms. The ^{31}P-^{13}C couplings (Fig 1) and the ^{13}C chemical shifts were obtained from the ^{13}C-FT proton noise decoupled NMR spectrum.

The assignment of C7 follows from its chemical shift and the assignment of C1 and C6 could be made because they bear no hydrogen atom (Fig 1c). Gray and Cremer[12] found a dihedral dependence of the $^{2}J_{PC}$ coupling constant. On this basis one predicts for C6 a small coupling constant of 0–5 Hz (Found 0 Hz) and for C2 a large coupling constant of 27–37 Hz (Found 36·5 Hz). The assignment of C3, C4 and C5 is arbitrary but probably there is a $^{3}J_{PC}$ spin coupling of 13·9 Hz (Fig 1b) analogous to triphenylphosphine.[13] However, contrary to triphenylphosphine positions 3 and 5 are not equivalent in **1**, and, in fact, we do find only one of these carbon atoms coupled to phosphorus; apparently, there is also a dihedral dependence in the $^{3}J_{PC}$ coupling.

The ^{31}P NMR signal of **1** appears at high field [$\delta^{31}P = +64{\cdot}8$ ppm ($CDCl_3$, external H_3PO_4)] probably because the free electron pair has a high s-character.[2,3] Calculation of the C–P–C bond angle in **1** from its ^{31}P chemical shift gave 93° using the formula of Parks[14] and 99° using the tables of Van Wazer.[15] Both angles are smaller than the C–P–C bond angle of 103° in triphenyl phosphine.[16] The chemical shift is intermediate between those reported for diphosphatriptycene (+43)[3] and azaphosphatriptycene (+80),[2] reflecting a progressive decrease of the C–P–C bond angle. This trend is expected if one considers the effect of bond angles and bond distances of the second bridgehead atom (i.e. P, C, and N, resp.) on the bond angles at the P atom.

The investigation of the nucleophilicity of **1** is of interest because arsatriptycene[1] reacts with great difficulty with electrophilic reagents whereas azaphosphatriptycene[2] and diphosphatriptycene[3] do react with methyl iodide or benzyl bromide. As phosphines are generally more nucleophilic than arsines,[17] we expected that contrary to arsatriptycene **1** could be alkylated, although less readily than triphenylphosphine.

Reaction of **1** with an excess of methyl iodide or benzyl bromide gave the quaternary salts **8** and **9**, respectively. In parallel experiments conducted with **1** and triphenylphosphine at 30° in excess methyl iodide, **8** was formed more slowly than methyltriphenylphosphonium iodide by about one



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8: R = Me, X = I
9: R = $CH_2C_6H_5$, X = Br
10: R = H, X = SO_3F

order of magnitude. Hendrickson *et al*[18] found that the chemical shift and the phosphorus splitting constant are related to the amount of s-character in the σ-orbital bonding the methyl group to phosphorus (Table 1).

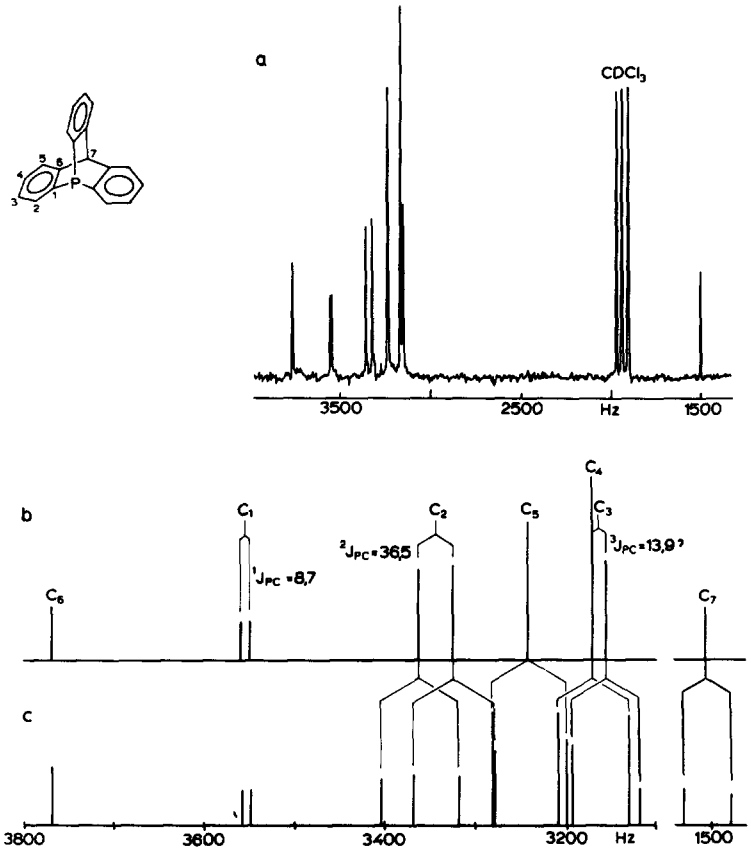

Fig 1. (a) 25·2 MHz proton noise decoupled, natural abundance ^{13}C-FT NMR spectrum (2000 pulses) of phosphatriptycene (1) (7% w/w solution in $CDCl_3$, 10 mm tube). Frequencies are downfield from internal TMS. (b) Line spectrum of a. (c) Off-resonance proton decoupled ^{13}C-FT line NMR spectrum.

In **8** we believe that there is a higher *p*-contribution from phosphorus to the P-aryl bonds than in the methyltriphenyl phosphonium salt because of the smaller C–P–C angle (pp. 141–142); consequently there should be a higher s-character of the P-methyl bond. This is in accordance with the greater phosphorus coupling constant in **8** and **9** and with the chemical shift (Table 1).

The ^{31}P NMR signal of **8** [δ ^{31}P = +2·4 ppm (CF_3COOD, external H_3PO_4)] appears also at higher field than that of triphenylmethyl phosphonium iodide (^{31}P = −19·4) in analogy with P-methyl-azaphosphoniatriptycene iodide.[2]

Table 1.

	δ_{H_α} (ppm)	$^2J_{PH}$	Amount of s-character
$(CH_3)_3P$	0·89	2·7	little
$(CH_3)_4P^+X^-$	2·47	14·4	25%
$(C_6H_5)_3CH_3P^+X^-$	3·12	13·2	<25%
8	3·35	16·0	>25%
9	5·36	16·0	>25%

Compound **1** was protonated in fluorosulfonic acid to the corresponding phosphonium salt **10** which had $^1J_{PH}$ = 568 Hz. The magnitude of the one bond coupling constant $^1J_{PH}$, has been related to the amount of s-character in the phosphorus orbital used for bonding to hydrogen.[19,20] The $^1J_{PH}$ coupling in the PH_4^+ cation is 548 Hz[19] and the phosphorus is expected to be sp^3 hybridized. Contrary to other phosphonium[19] ions the value of $^1J_{PH}$ in **10** indicates more than 25% s-character in the PH bond which confirms the interpretation of the NMR-results obtained with **1** and **8**.

When **1** is standing for two weeks in a chloroform solution about 20% has reacted with oxygen to phosphatriptycene oxide (**3**). In solid state **1** is less air-sensitive.

EXPERIMENTAL

M.ps are uncorrected. Mass spectra were recorded with a Varian Mat CH5 spectrometer and ^{1}H NMR spectra with a Varian A-60 spectrometer and with a Varian XL-100/12 WG spectrometer. Chemical shifts are given in δ (ppm) from internal TMS. The ^{13}C-FT noise decoupled NMR spectrum (locked deuterium) was recorded with a Varian XL-100/12 WG spectrometer operating at a

frequency of 25·2 MHz. The number of accumulated pulses were 2000 with a pulse delay of 5 sec. The ^{31}P-NMR spectra were recorded with a Varian XL-100/FT spectrometer operating at a frequency of 40·5 MHz. The IR spectra were recorded with a Perkin-Elmer spectrophotometer and the UV spectrum with a Perkin-Elmer spectrophotometer, model 137. Elemental analyses were performed under supervision of Mr. W. J. Buis at the Micro-analytical Department of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

M	M-H	M-2H	M-3H	M-4H	
272 (100)	271 (85)	270 (54)	269 (13)	268 (20)	239 (31)
136 (8)	135 1/2 (9)	135 (30)	134 1/2 (7)	134 (18)	
90 2/3 (0·1)	90 1/3 (0·1)	90 (0·4)	89 2/3 (0·1)	89 1/3 (0·4)	

9 - *Hydroxy* - 10 - *phenyl* - 9,10 - *dihydrophosphaanthracene* - 9 - *oxide* (**2**). Hydrogen peroxide was added slowly to a boiling mixture of **5** (0·50 g) in 2N NaOH. After refluxing for 1 h, the mixture was filtered. **2** was precipitated by adding 2N HCl, and was recrystallized from EtOH yielding 0·25 g of white crystals m.p. 246–248°, yield 50% [Found: C, 73·82; H, 5·22; P, 9·74; $C_{19}H_{15}PO_2$ (M = 306·28) requires: C, 74·50; H, 4·94; P, 10·11%]; IR (KBr) cm^{-1}: 2300 (OH), 1170 (P═O). NMR (D_6DMSO), 8·3 (s, 1, P-OH), 8·05–7·75 (m, 2, aryl protons), 7·60–7·03 (m, 11, aryl protons), 5·66 (s, 1, methine proton). Mass spectrum *m/e* (%): 306 (100), 288 (58), 239 (23), 165 (23).

Attempts to prepare phosphatriptycene oxide (**3**) *from* 9 - *hydroxy* - 10 - *phenyl* - 9,10 - *dihydrophosphaanthracene* - 9 - *oxide* (**2**). Compound **2** (0·17 g) was heated *in vacuo* to 300° and another sample of **2** (0·060 g) to 360°. After cooling, the mixtures were analysed with preparative TLC (hexane/aceton, v/v 2:1; silicagel); **3** could not be detected.

Compound **2** (0·22 g) and polyphosphoric acid (15 g) were heated at 150° for 50 min under N_2 and then poured into 300 ml ice water. The resulting ppt was filtered off, washed with water and analysed with preparative TLC (hexane/aceton, v/v 2:1; silicagel); **3** could not be detected.

9 - (o - *Chlorophenyl*) - 9,10 - *dihydrophosphaanthracene* (**6**). A soln of the Grignard compound (3 mmol) prepared from *o*-chlorobromobenzene[21] (2 g) and Mg (350 mg) in 50 ml dry ether, was added under N_2 at −70° in 1 h to a soln of **4**[7] (1·6 mmol). After stirring overnight at room temp, a few drops of dry MeOH were added to the red soln, which decolourized immediately; then the soln was evaporated *in vacuo*. Sublimation of the residue (130°/0·01 mm) yielded **6** (0·27 g, 52%), m.p. 104–106°. [Found: C, 73·85; H, 4·76; P, 9·80; Cl, 11·38. $C_{19}H_{24}ClP$ (M = 308·72) requires: C, 73·91; H, 4·57; P, 10·03; Cl, 11·49%]; NMR ($CDCl_3$): 7·95–7·50 (m, 2, aryl protons), 7·50–6·67 (m, 10, aryl protons), 3·91 (d, 2, CH_2, $^3J_{PH}$ = 4 Hz). Mass spectrum *m/e* (%): 310 (24), 308 (72), 273 (24), 272 (10), 239 (13), 197 (45), 196 (65), 165 (100).

9,10 - *Dihydro* - 9,10 - o - *benzeno* - 9 - *phosphaanthracene* (*phosphatriptycene*) (**1**). n-BuLi (18 mmol) was added at 0° under N_2 to a soln of diisopropylamine (23 mmol) in dry ether (25 ml) and after stirring for 15 min a soln of **6** (3·8 mmol) in dry THF (1 ml) was added. The mixture was boiled under reflux (3 days), water was added, and the ethereal layer was separated, dried, and evaporated, leaving a residue which on sublimation (150°/0·01 mm) and recrystallization (EtOH) afforded **1** (360 mg, 35%), m.p. 242–243°; addition of triptycene (m.p. 252–253°) gave the following mixed m.ps: 67% **1**: m.m.p. 232–233°; 50% **1**: m.m.p. 234–235° [Found: C, 83·42; H, 5·07; P, 11·56, $C_{19}H_{13}P$ (M = 272·27) requires: C, 83·81; H, 4·81; P, 11·38%]; IR (KBr), ν_{max} in cm^{-1}: 3075 (m), 3010 (m), 2950 (m), 1450 (s), 1280 (m), 1130 (s), 870 (m), 765 (s), 745 (s), UV (96% ethanol), λ_{max} (log ϵ): 268 (3·04), 278 sh (2·86). NMR ($CDCl_3$) δ: 8·01–7·70 (m, 3, aryl protons), 7·70–7·41 (m, 3, aryl protons), 7·41–7·02 (m, 6, aryl protons), 5·62 (s, 1, methine proton). Mass spectrum *m/e* (%):

9,10 - *Dihydro* - 9,10 - o - *benzeno* - 9 - *methyl* - 9 - *phosphoniaanthracene iodide* (**8**). A carius tube was charged with **1** (78 mg), MeI (5 ml) and dry ether (5 ml). After a few hours at 45° the tube was opened and the ppt was filtered off. To a soln of this ppt in alcohol/water a saturated soln of KI in water was added. A ppt formed, which was filtered off and washed with water, affording **8** (84 mg; 72%), m.p. 185° (dec). [Found: C, 58·63; H, 4·47; P, 7·59; I, 28·70. $C_{20}H_{16}PI$ (H = 414·20); requires: C, 57·99; H, 3·89; P, 7·48; I, 30·64%]; NMR (CF_3COOD): 8·27–7·22 (m, 12, aryl protons), 6·12 (s, 1, methine proton), 3·35 (d, 3, CH_3, $^2J_{PH}$ = 16·0 Hz).

9,10 - *Dihydro* - 9,10 - o - *benzeno* - 9 - *benzyl* - 9 - *phosphoniaanthracene bromide* (**9**). A mixture of **1** (38 mg) and benzyl bromide (5 ml) was warmed to 110° for 3 h. The ppt was filtered off and washed with dry ether yielding **9** (56 mg, 91%), m.p. 316° (dec). [Found: C, 70·06; H, 4·71; P, 7·11; Br, 17·44. $C_{26}H_{20}PBr$ (M = 443·30); requires: C, 70·44; H, 4·55; P, 6·99; Br, 18·03%]; NMR (CF_3COOH): 8·15–7·20 (m, 17, aryl protons), 6·17 (s, 1, methine proton), 5·36 (d, 2, CH_2, $^2J_{PH}$ = 16·0 Hz).

9,10 - *Dihydro* - 9,10 - o - *benzeno* - 9 - *phosphoniaanthracene fluorosulfate* (**10**). Fluorosulfonic acid (0·3 ml) was added under N_2 to **1** (65 mg) and after a few min a yellow soln developed. NMR (HSO_3F, external TMS): 11·20–10·64 (s, HSO_3F), 9·00 (d, 1, proton at phosphorus, $^1J_{PH}$ = 568 Hz), 8·60–7·20 (m, 12, aromatic protons), 6·22 (s, 1, methine proton).

9,10 - *Dihydro* - 9,10 - o - *benzeno* - 9 - *phosphaanthracene* - 9 - *oxide* (*phosphatriptycene oxide*) (**3**). A soln of **1** (200 mg) in $CDCl_3$ (1 ml) was kept standing for 2 weeks in the air. **3** was obtained by preparative TLC (hexane/aceton, v/v 2:1; silicagel) as a white ppt. Recrystallization from alcohol/water yielded white crystals of **3** (20%), m.p. 281–282°. [Found: C, 78·84; H, 5·17; P, 10·97; $C_{19}H_{13}PO$ (M = 288·26); requires: C, 79·16; H, 4·54; P, 10·74%]; IR (KBr), ν_{max} in cm^{-1}; 1240 (s) (P═O); NMR ($CDCl_3$): 8·42–7·83 (m, 3, aryl protons), 7·83–7·09 (m, 9, aryl protons), 5·48 (s, 1, methine proton). Mass spectrum *m/e* (%): 288 (46), 287 (7), 270 (100), 268 (10), 240 (17), 239 (38).

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