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9-PHENYL-9-BENZYL-9-PHOSPHAANTHRACENE, A TRICYCLIC λ^5-PHOSPHORIN

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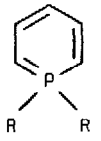
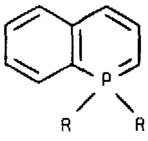
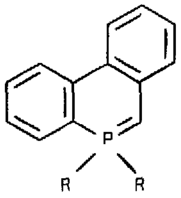
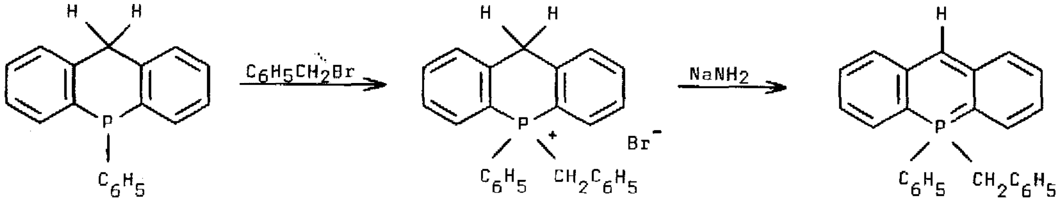
1,1-Disubstituted phosphabenzenes (λ^5-phosphorins; I) have been synthesized from the corresponding phosphonium salts by deprotonation[1] and from substituted λ^3-phosphorins by radical[2] or anionic addition[3] reactions. 1,1-Disubstituted-1-phosphanaphthalenes (II) could only be synthesized from the corresponding phosphonium salts[4]; formation via λ^3-phosphanaphthalenes has failed so far[5,6]. One tricyclic λ^5-phosphaphenanthrene (III) has been studied in solution[7]. We wish to report the synthesis and some reactions of 9-phenyl-9-benzyl-9-phosphaanthracene (IV).


I


II


III

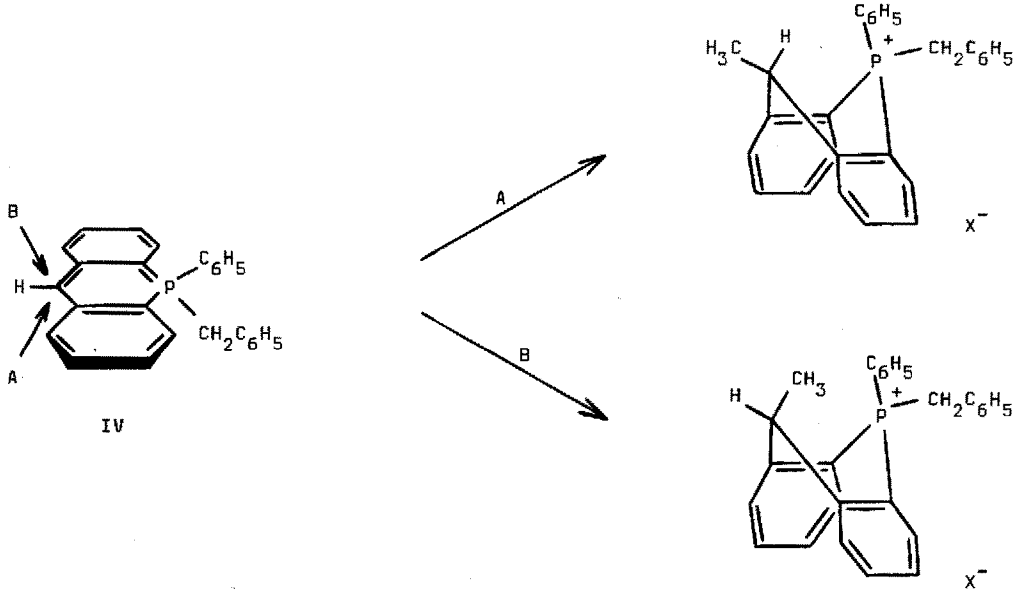
9-Phenyl-9,10-dihydro-9-phosphaanthracene (V)[8] reacted with benzyl bromide at 80° to give the phosphonium salt VI (80% yield; m.p. 325 - 326°). NMR[9] (CF_3COOH): 8.11 - 7.05 (m, 16, aryl protons), 6.71 - 6.49 (m, 2, aryl protons), 4.44 (d, 2, CH_2, $^2J_{P-H}$ = 14 Hz), 4.15 (dd, 1, H_{10}, $J_{10,10'}$ = 21 Hz, $^4J_{P-H}$ = 2 Hz), 2.93 (dd, 1, $H_{10'}$, $J_{10,10'}$ = 21 Hz, $^4J_{P-H}$ = 4 Hz). UV (ethanol), λ_{max} (ε): 284 (4530), 276 (5500), 269 (5100), 261 (4980), 255 (5160).



V VI IV

A suspension of VI and sodium amide in THF was stirred for 48 hr at 50° and after filtration the red solution was evaporated to dryness and the residue was extracted with cyclohexane. On evaporation, the cyclohexane solution yielded IV (43% yield; m.p. 161 - 164°). NMR (C_6D_6): 7.78 - 6.31 (m, 18, aryl protons), 5.75 (s, 1, methine proton), 3.36 (d, 2, CH_2, $^2J_{P-H}$ = 12.5 Hz) and a weak unidentified signal at 3.59 (d, J = 3 Hz). UV (THF), λ_{max} (ε): 582 (2930), 495 (7920), 392 (6300), 277 (14200). Mass spectrum m/e (%): 364.1388 (20), $M^{+\cdot}$ (calcd. for $C_{26}H_{21}P$: 364.1381), 273 (100), $(M - CH_2C_6H_5)^+$, 196 (44), $(M - CH_2C_6H_5 - C_6H_5)^{+\cdot}$.

For structural identification IV in THF was reacted with methyl iodide, resulting in the instantaneous precipitation of the expected phosphonium salt VIIa. NMR (CF_3COOH): 8.17 - 7.41 (m, 13, aryl protons), 7.41 - 6.95 (m, 3, aryl protons), 6.95 - 6.60 (m, 2, aryl protons), 4.50 (d, 2, CH_2, $^2J_{P-H}$ = 13.5 Hz), 4.50 - 3.98 (m, 1, methine proton), 1.46 [d, 1.5, CH_3 (A?), $^3J_{H-H}$ = 7.1 Hz], 0.77 [d, 1.5, CH_3 (B?), $^3J_{H-H}$ = 7.1 Hz].

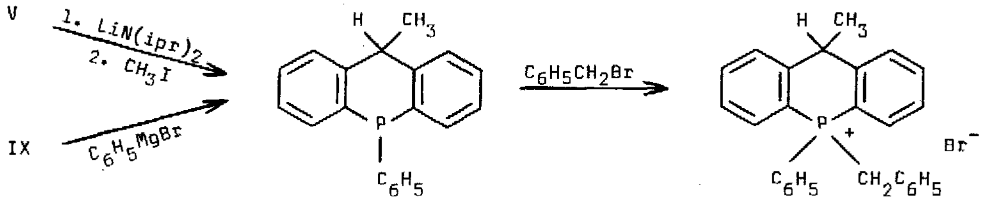


IV

VII a X = I

VII b X = Br

It is obvious that compound VIIa consisted of two stereoisomeric forms present in about equal amount. Their formation can be explained by the assumption that in the electrophilic attack of methyl iodide, there is practically no preference for route A or B; it can therefore be considered as chemical evidence for IV to be a planar, delocalized π-electron system[10]. This interpretation (and the structure of VIIa) is supported by the observation that independent synthesis of VIIb by two different routes furnishes different amounts of the two stereoisomers of VII. Reaction of lithium diisopropylamide with V followed by addition of methyl iodide yielded only one isomer of VIII (80% yield). NMR ($CDCl_3$): 7.82 - 6.90 (m, 13, aryl protons), 3.94 (q, 1, methine proton, $^3J_{H-H}$ = 7.1 Hz), 1.36 (d, 3, CH_3, $^3J_{H-H}$ = 7.1 Hz). Reaction of VIII with benzyl bromide afforded VIIb. NMR (CF_3COOH): identical with that of VIIa, except for only one methyl signal at 1.46 ppm.

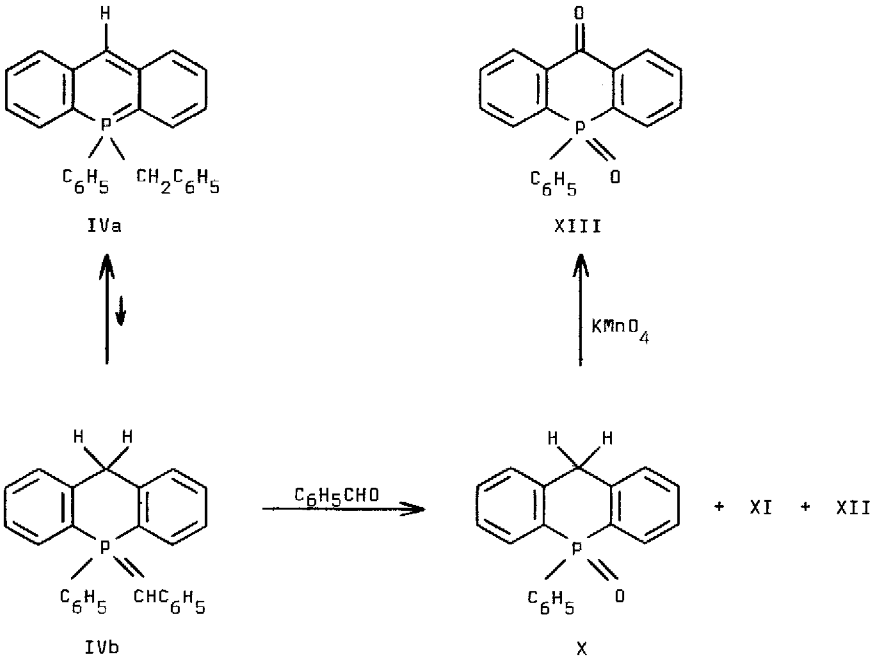


VIII

VIIb

Reaction of 9-chloro-10-methyl-9,10-dihydro-9-phosphaanthracene (IX)[11] with phenylmagnesium bromide afforded VIII (65% yield, m.p. 103 - 107°) as a mixture of both stereoisomers, as indicated by its NMR spectrum ($CDCl_3$): 7.82 - 6.80 (m, 13, aryl protons), 4.28 (q, 0.66, methine proton, $^3J_{H-H}$ = 7.1 Hz), 3.94 (q, 0.34, methine proton, $^3J_{H-H}$ = 7.1 Hz), 1.42 [dd, 2, CH_3, $^3J_{H-H}$ = 7.1 Hz, $^5J_{P-H}$ (?) = 1 Hz], 1.36 (d, 1, CH_3, $^3J_{H-H}$ = 7.1 Hz). Reaction of VIII with benzyl bromide yielded VIIb. NMR (CF_3COOH): identical with that of compound VIIa, but as in VIII the isomer ratio was A : B = 1 : 2.

The planar, delocalized structure of I and II has been conclusively confirmed by X-ray structure determination[12] and NMR spectroscopy[13]. Chemical evidence for "aromaticity" was derived from the fact that both types of compounds, although being formally phosphorus ylids, do not undergo the Wittig reaction with carbonyl derivatives; however with III a Wittig reaction did occur. When benzaldehyde was added to IV in THF the red colour slowly disappeared; after standing overnight the solution was evaporated to dryness and the residue was separated by TLC (hexane/acetone = 1 : 1) yielding X (80 - 90%), cis-stilbene (XI) (25 - 35%) and trans-stilbene (XII) (40 - 50%). Compound X was further characterized by oxidation with potassium permanganate to XIII, which was identical with an authentic sample[8].



The course of the reaction can be explained if one assumes an equilibrium between the tautomeric forms IVa and IVb; this equilibrium of IV lies strongly on the side of IVa, as evidenced by the NMR spectrum, but the weak "unidentified" signal at 3.59 ppm might be derived from the two protons at $C_{(10)}$ of IVb (estimated 10%). Product formation may then take place by a normal Wittig reaction from IVb and a gradual reestablishment of the equilibrium between IVa and IVb.

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