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3-METHYL-2-PHOSPHANAPHTHALENE

H.G. de Graaf, J. Dubbeldam, H. Vermeer, and F. Bickelhaupt

Scheikundig Laboratorium der Vrije Universiteit

De Lairessestraat 174, Amsterdam-Z, The Netherlands

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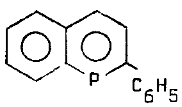
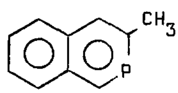
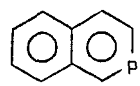
Phosphorus analogues of benzene[1,2], anthracene[3] and phenanthrene[4] have been known for several years. The corresponding analogues of naphthalene, however, appeared to be less readily accessible. Recently, Märkl and Heier reported the synthesis of a derivative of 1-phosphanaphthalene, 2-phenylbenzo[b]phosphorin (I)[5]. By a different approach, namely using our previously developed method of HCl-elimination from a dihydroprecursor[3,4] in the final step, we have prepared the first derivative of 2-phosphanaphthalene, 3-methylbenzo[c]phosphorin (II); similarly, evidence was obtained for the formation of the unsubstituted parent heterocycle III in solution.


I


II


III

Starting from diethyl benzylphosphonite (IVa) we obtained the ketophosphinic acid Va (m.p. 204-205° C) in analogy to Henning's synthesis of Vb from IVb[6]. Reduction of Va with $NaBH_4$ in H_2O and dehydration by heating with 10% H_2SO_4 yielded VI (53% yield; m.p. 200-202° C); ^1H NMR spectrum (D_6-DMSO): δ 7.35-7.10 (m, 4.5 H, arom. + 0.5 vinylic H), 7.10 (s, 1H, -OH), 6.63 (q, 0.5 H, 0.5 vinylic H), 3.12 (d, 2H, $-CH_2-$), 1.95 (d of d, 3H, CH_3). Reaction with thionyl chloride converted VI into its acid chloride which was reduced at -15° C by $LiAlH_4$ in ether to the secondary phosphine VII which was purified by molecular distillation (21% yield; b.p. ca. 80° C at 10^{-1} Torr.); NMR spectrum ($CDCl_3$, external TMS): δ 7.70-7.40 (m, 4H, arom.), 7.22 (d of q, $^3J_{PH}$ 9 Hz, $^3J_{HH}$ 1.5 Hz, 1H, vinylic H), 4.26 (broad s, 1H, P—H), 3.32 (d, $^2J_{PH}$ 7.5 Hz, 2H, $-CH_2-$), 2.54 (d of d, $^3J_{PH}$ 12 Hz, $^3J_{HH}$ 1.5 Hz, 3H, CH_3). The singlet for the phosphine proton is remarkable; however, its presence followed unambiguously from the IR spectrum (ca. 8% in $CHCl_3$), which has a P—H stretch vibration at 2250 cm^{-1} . By reaction with phosgene in toluene (during one hour slowly warmed from -196° C to room temperature), VII was converted to the corresponding chlorophosphine which was not isolated[7] but treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in a high vacuum sealed vessel. Filtration from DBU.HCl, evaporation of the filtrate, extraction of the residue with n-hexane and vacuum sublimation of the residue yielded white crystals of II (ca. 10% yield from VII, m.p. 64.5-69° C).

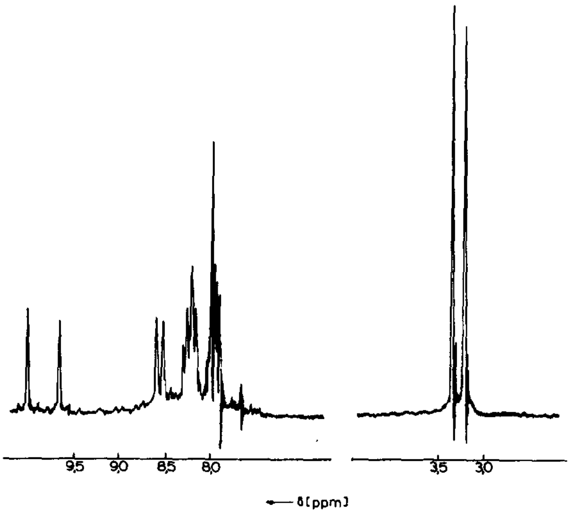
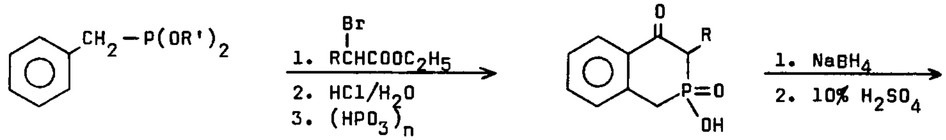


Fig. 1. 100 MHz NMR spectrum of II in $CDCl_3$

The structure of II follows from the elemental analysis and from its spectral data. NMR spectrum (see Fig. 1) (100 MHz, $CDCl_3$, external TMS): 9.84 (d, $^2J_{PH}$ 35 Hz, 1H, H^1), 8.57 (d, $^3J_{PH}$ 7.5 Hz, 1H, H^4), 8.35-7.85 (m, 4H, benzo-C_6H_4), 3.30 (d, $^3J_{PH}$ 13.5 Hz, 3H, CH_3); chemical shifts and coupling constants are in accordance with those of Märkl[8] and Ashe[2] for phosphabenzenes. UV spectrum (diethyl ether): λ_{max} 252 nm (ε = 28850), 304 nm (6630), 343 nm (450), and 360 nm (270); the spectrum disappeared rapidly on admission of air. The general agreement with UV spectra of naphthalene and isoquinoline derivatives is obvious; however, there is no simple trend in λ_{max} or in ε. Mass spectrum: m/e 160, 100% ($M^{+\cdot}$); 128, 94% [$(M-PH)^{+\cdot}$ = $C_{10}H_8^{+\cdot}$]; 80, 12% (M^{2+}).



IVa : R' = C_2H_5

IVb : R' = $CH(CH_3)_2$

Va : R = CH_3

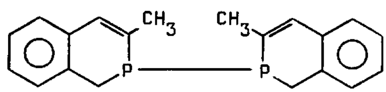
Vb : R = H

VI

VII

The residue from the sublimation of II was a white, crystalline, air sensitive material (m.p. 92-96° C) which has not yet been fully characterized. Its mass spectrum [m/e 322, 30% ($M^{+\cdot}$); 162, 100%; 161, 66%; 160, 74%; 128, 78%], IR spectrum (absence of P-H stretch vibrations) and oxidation with warm dilute HNO_3 to VI point to structure VIII.

VIII



In a similar fashion we tried to prepare III; due to lack of material and to instability of intermediate products the secondary phosphine analogous to VII could not be purified. Consequently, its reaction with $COCl_2$ and DBU led to a complex mixture from which no III could be isolated so far; however, its presence in solution follows from the appearance of a maximum at 305 nm on addition of DBU to the chlorophosphine.

References

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