Tetrahedron Letters No. 41, pp 3715 - 3716, 1976. Pergamon Press. Printed in Great Britain.

2,3,5,6-TETRAKIS(TRIFLUOROMETHYL)-1,4-DIPHOSPHABENZENE

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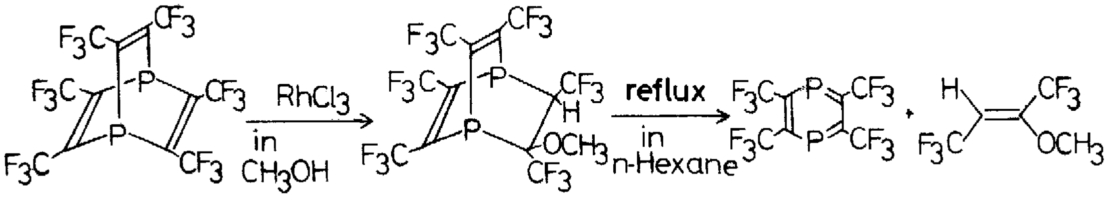
(Received in Japan 10 July 1976; received in UK for publication 23 August 1976)

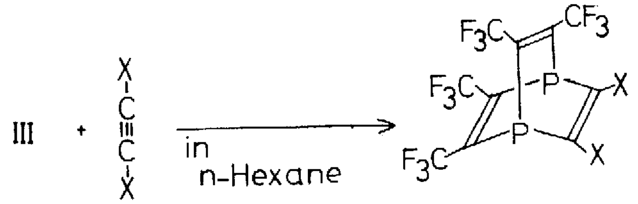
Synthesis of phosphabenzenes, phosphorus analogs of benzene,[1,2] and 2,6-diphenyl-1-aza-4-phosphabenzene[3] were reported. In this report, we should like to report synthesis of a derivative of the 1,4-diphosphabenzene.

Treatment of 2,3,5,6,7,8-hexakis(trifluoromethyl)-1,4-diphosphabicyclo-[2.2.2]octa-2,5,7-triene (I)[4] with rhodium trichloride (0.4 eq.) in methanol at room temperature for several days gave 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene (II) in 55% yield, mp 68-70° (colorless crystals from n-pentane); ir (KBr) 1600 cm^{-1}; uv (MeOH) 243 (ε = 1650), 332 nm (1010); ^{1}H-nmr ($CDCl_3$)δ 3.37 (3H, s, OCH_3), 2.8 (1H, q, CH, J_{HF} = 9Hz); ^{19}F-nmr ($CDCl_3$)[5] ppm -4.8 (15F, m), 3.6 (3F, m). To our great interest, the mass spectrum of II shows no peak of molecular ion but shows peaks of m/e 386 [corresponding to 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (III)] and 194 [corresponding to 1,1,1,4,4,4-hexafluoro-2-methoxybutene-2 (IV)]. This fact suggests that II could be a precursor of III. Actually, III and IV were obtained by refluxing II in hexane solution in a stream of argon. Compound IV was collected in a trap connected to the top of the reflux-condenser and cooled at -78°. Compound III was obtained in the hexane solution in the reaction vessel. The structure of IV was determined by comparison of the ^{1}H- and ^{19}F-nmr spectra with those of an authentic sample.[6] Small coupling constant of the two CF_3 shows that IV is trans form. The uv spectrum of III shows a strong peak at 282 nm ($\varepsilon >$ 4000-5000 in hexane). It is impossible to measure the accurate ε value because of the unstability of III. The ^{19}F-nmr signal of the four equivalent CF_3 groups appears at -6.6 ppm (J_{PF} = 66 Hz). The mass spectrum of III after evaporation of hexane in argon stream shows relatively weak molecular ion (m/e 386) and a strong peak (m/e 317 (M^+-CF_3)). The datum of the uv spectrum suggests that the structure of III is that of 1,4-diphosphabenzene.

This suggestion is supported by the reaction of III with hexafluorobutyne-2, dimethylacetylene, and dimethylacetylene dicarboxylate to give 1:1 adducts of I, V, and VI, respectively. V: mp 152.5-153° (colorless crystals by sublimation); ir (KBr) 1600, 1640 cm^{-1}; uv (MeOH) 272 (ε = 860), 326 nm (610); ^1H-nmr (($(CD_3)_2CO$)δ 2.43 (6H, d, Me, J_{PH} = 43 Hz); ^{19}F-nmr $(CD_3)_2CO$ ppm -6.3 (12F, d, J_{PF} = 37 Hz); mass spectrum m/e 440 (M^+); high mass spectrum calcd for $C_{12}H_6F_{12}P_2$ 439.975, found 439.975. VI: mp 108-110° (pale yellow crystals by sublimation); ir (KBr) 1600, 1740 cm^{-1}; uv (MeOH) 317 nm (shoulder); ^1H-nmr ($CDCl_3$)δ 3.90 (6H, s, OMe); ^{19}F-nmr ($CDCl_3$) ppm -6.6 (12F, d, J_{PF} = 40 Hz); mass spectrum m/e 528 (M^+); high mass spectrum calcd for $C_{14}H_6F_{12}O_4P_2$ 527.955, found 527.953. These results are comparable to the reaction of phosphabenzenes with acetylenes to form the corresponding 1-phosphabarrelene compounds.[7]



I II III IV



I, X = CF_3 (52%)

V, X = CH_3 (79%)

VI, X = $COOCH_3$ (51%)

REFERENCES

1) A.J. Ashe, III, J. Amer. Chem. Soc., 93, 3293 (1971).
2) G. Märkl, Angew. Chem. Int. Ed., 5, 846 (1966); G. Märkl, F. Lieb, and A. Merz, ibid., 6, 458, 944 (1967).
3) G. Märkl and D. Matthes., Angew. Chem., 84, 1069 (1972).
4) C.G. Krespan, J. Amer. Chem. Soc., 83, 3432 (1961).
5) Benztrifluoride: 0 ppm as an internal standard.
6) R.N. Haszeldine, J. Chem. Soc., 1952, 3490. Haszeldine did not discuss the stereochemistry of the olefin. Investigation of the nmr spectrum shows that the olefin obtained by his method contains a small amount of cis-isomer.
7) A.J. Ashe, III and M.D. Gordon, J. Amer. Chem. Soc., 94, 7596 (1972).