Tetrahedron Letters No. 35, pp 3057 - 3058, 1977. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF TRIFLUOROMETHYLATED 1,4-DIPHOSPHANORBORNADIENE

Yoshiro Kobayashi*, Itsumaro Kumadaki, Hiroshi Hamana, and Shomi Fujino
Tokyo College of Pharmacy, Horinouchi, Hachioji-shi, Tokyo 192-03, Japan
(Received in Japan 1 June 1977; received in UK for publication 8 July 1977)

In the previous papers,[1,2] we reported the derivation of 2,3,5,6-tetrakis-(trifluoromethyl)-1,4-diphosphabenzene (I), the first example of diphospha analogues of benzene, from 2,3,5,6,7,8-hexakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene (II). The compound I reacted as a diene with acetylenes, while II reacted as a dienophile in the Diels-Alder reaction[2]. On the other hand, Krespan[3] reported that II shows no reaction of trivalent phosphorus because of the steric effect of the trifluoromethyl groups. The fact that I is very sensitive to air and decomposes through monooxide might be ascribed to the trivalent character of the phosphorus of I. In this report, another reaction characteristic of the trivalent phosphorus and the formation of a novel ring system, 1,4-diphosphanorbornadiene, will be discussed.

Heating I with carbon tetrachloride in a sealed nmr tube at 130°C caused disappearance of the peak ascribed to I and appearance of two new doublets[4] (-8.0 and -10.2 ppm) in ^{19}F-nmr spectrum, while no change was observed after heating II at 140°C. Work-up of the reaction mixture gave a diphosphanorbornadiene compound, 7,7-dichloro-2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.1]hepta-2,5-diene (IV), to which one of the two doublets was assigned. IV; mp 39-39.5°; ir (KBr) 1600 cm^{-1} (C=C), ^{19}F-nmr (CCl_4) ppm -8.00 (6F, 1/2 (J_{PF} + $J_{PF'}$) = 22.6 Hz), mass spectrum m/e 468 (M^+), high mass spectrum calcd. for $C_9Cl_2F_{12}P_2$: 467.866, found: 467.868, apparent yield 27.3%, (54.6% based on the mechanism proposed below).

The mechanism for formation of IV is assumed by analogy with the reaction of triphenylphosphine with carbon tetrachloride[5] as shown in Chart 1. Formation of V was supported by the nmr spectrum of the reaction mixture: two doublets of nearly the same intensities appeared after heating, one of which was ascribed to IV and the other (-10.2 ppm, J_{PF} = 38.4 Hz) to V. The latter fell away rapidly after the tube was opened. This fact was in accordance with the expectation that a halophosphorous compound such as V should be unstable to air and moisture. Therefore, this reaction shows that I has the character of trivalent phosphorus. The compound IV is a new ring system containing two phosphorus atoms at the bridge-heads.

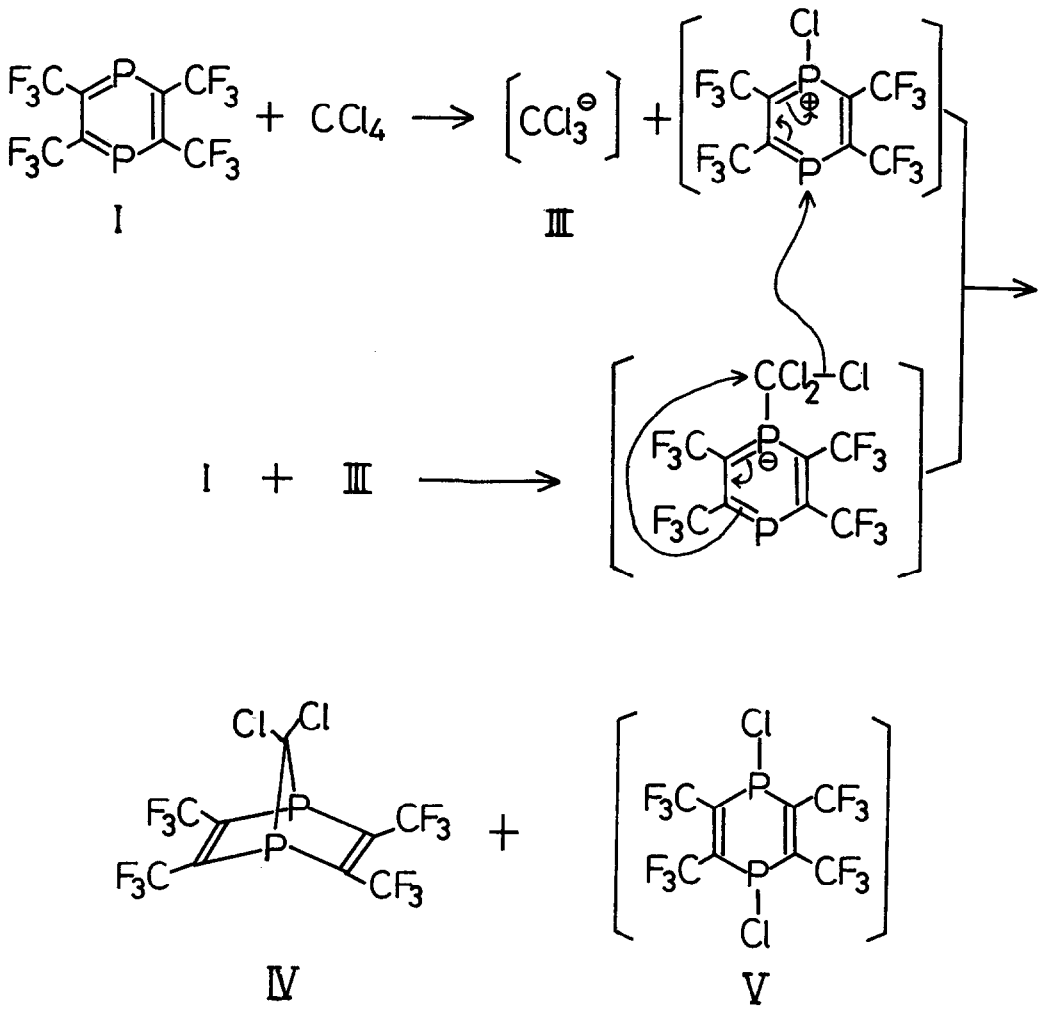

chart 1

References and Notes

1) Y. Kobayashi, I. Kumadaki, A. Ohsawa, and H. Hamana, Tetrahedron lett., 1976, 3715.
2) Y. Kobayashi, I. Kumadaki, Y. Hanzawa, H. Hamana, and S. Fujino, Tetrahedron Lett., 1976, 4815.
3) C. G. Krespan, J. Am. Chem. Soc., 83, 3432 (1961).
4) Benztrifluoride: +0 ppm as an internal standard.
5) I. M. Downie, J. B. Lee, and M. F. S. Matough, J. Chem. Soc., Chem. Comm., 1968,1350.