SYNTHETHIS AND REACTIONS OF 1,3,4,6-TETRAKIS(TRIFLUOROMETHYL-2,5-DIPHOSPHATRICYCLO[3.1.0.$0^{2,6}$]HEXENE-3

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In the study of the reactivity of 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (I), the phosphorus atom of I was found to have trivalent character. Photolysis of I gave 1,3,4,6-tetrakis(trifluoromethyl)-2,5-diphosphatricyclo[3.1.0.$0^{2,6}$]-hexene-3 (II), which formed 1:1 adduct with furan or 2,3-dimethylbutadiene. The isolation of II is the first example of a benzvalene analogue containing hetero atoms in the ring system.

1: The reaction of I with carbon tetrachloride gave 7,7-dichloro-2,3,5,6-tetrakis-(trifluoromethyl)-1,4-diphosphabicyclo[2.2.1]hepta-2,5-diene in 27.3% and an unstable compound which is assumed to be 1,4-dichloro-2,3,5,6-tetrakis(trifluoromethyl)-1,4-dihydro-1,4-diphosphabenzene.

2: Treatment of the methanol adduct (III) of 2,3,5,6,7,8-hexakis(trifluoromethyl)-1,4-diphosphabarrelene (IV) with excess sulphur gave IV and 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphospha-7-thiabicyclo[2.2.1]hepta-2,5-diene probably through I. Treatment of III with half molar equivalent of sulphur gave I and a compound which is assumed to be 3,4-bis(trifluoromethyl)-1,2,5-thiaphosphole.

3: The solution of I in perfluoropentane was sealed in a Pyrex tube under vacuum and irradiated with a high pressure mercury lamp for 72 hr. Separation of the reaction mixture by trap-to-trap distillation gave II. Compound III was found to give I at first and then II under the same condition as in the case of photolysis of I.

Compound II is thermally or photochemically isomerized to I, and its half life at 198°C in perfluorobenzene is about 75 min. The Diels-Alder reaction of II in pentane with furan or 2,3-dimethylbutadiene gave 1:1 adduct at room temperature.