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1,3-DIPOLAR CYCLOADDITION REACTIONS OF A DIPHOSPHABARRELENE

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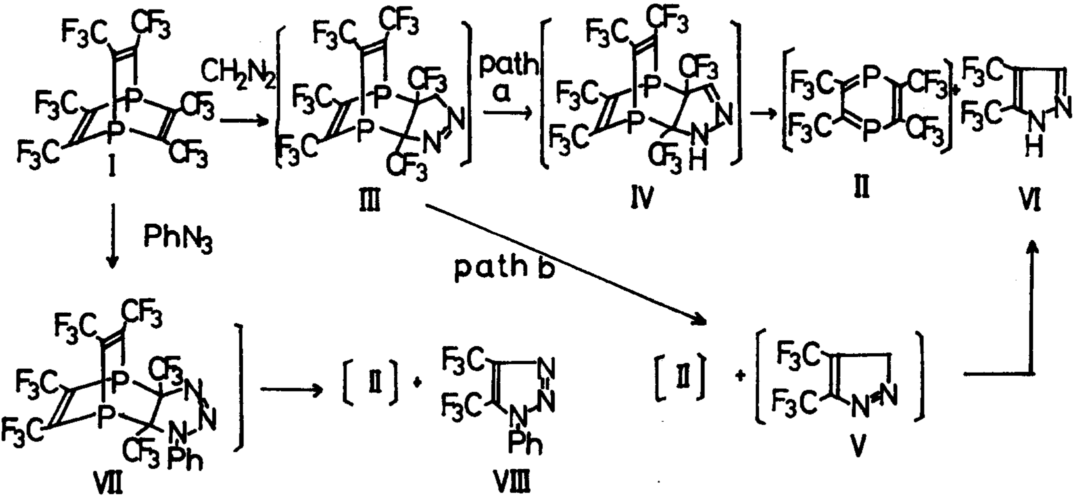
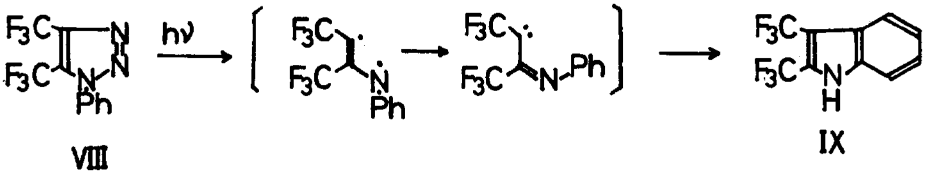
On studying the reactivity of a diphosphabarrelene, 2,3,5,6,7,8-hexakis-(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene (I), we succeeded in the syntheses of 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (II)[1] and a new cage compound with two phosphorus atoms.[2]

In this paper, we wish to report 1,3-dipolar cycloaddition reactions of the diphosphabarrelene (I) with diazomethane and phenyl azide. Reaction of I with diazomethane at room temperature gave 4,5-bis(trifluoromethyl)pyrazole (VI) quantitatively. The fact that I did not react with dimethylacetylene even at 200° shows that there is no equilibrium between I, and II and hexafluorobutyne-2. Therefore, I must have reacted at first with diazomethane to give 1,3-dipolar cycloadduct (III) and then III dissociated readily into II and VI via path a or path b. This reaction is one of the rare examples[3] of a mild cycloreversion of a 1,3-dipolar adduct obtained from a diazoalkanes. Similarly, the reaction of I with phenyl azide did not give the primary adduct (VII), but 1-phenyl-4,5-bis(trifluoromethyl)-1,2,3-triazole (VIII) quantitatively. The structures of VI and VIII were determined by comparison with the authentic samples which were obtained by the reactions of hexafluorobutyne-2 with diazomethane[4] and phenyl azide.[5] Therefore, it is evident that I is a good 1,3-dipolarophile. The adducts (III and VII) were very unstable and easily dissociated into II, VI, and VIII. II is very reactive and seemed to be decomposed by the reaction with 1,3-dipolar compounds.

Further, irradiation of VIII in n-pentane solution (6) gave 2,3-bis(trifluoromethyl)indole (IX) (43.7%) with the recovery of the starting material (22.6%).

The structure of IX was determined by comparison with the authentic sample.(5) Photochemical decomposition of 1-phenyl-1,2,3-triazole derivatives was reported to give indole derivatives and ketenimine derivatives,(7) but in this case the ketenimine derivative was not obtained, possibly because of the electronic effect of the trifluoromethyl group.





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