ISOLATION AND CHARACTERIZATION OF A THIADIPHOSPHIRANE

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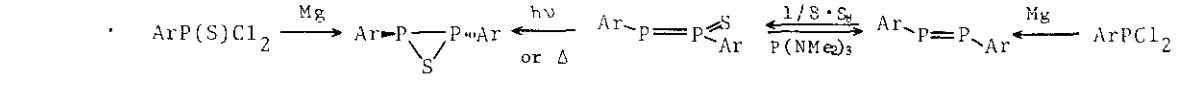
Phosphorus containing small ring compounds, especially three-membered ring compounds, are of current interest. By introducing an extremely bulky group into a molecule, we were successful in the preparation and characterization of *E*-2,3-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,3-thiadiphosphirane (2) as a stable compound by the following two different methods.

a) The phosphonothioic dichloride (1) was allowed to react with magnesium in tetrahydrofuran to give 2 in 54% yield as a stable crystalline material (mp 131.5 - 132°C, δ_P -65.1 ppm). 2 was thermally and photochemically stable and insensitive to atmospheric moisture and oxygen for a long period of time.



1 2 3 4 5

(Ar = 2,4,6-*t*-$Bu_3C_6H_2$)

b) The orange diphosphene (4, mp 175 - 176°C, δ_P 492.4 ppm), obtained from the phosphonous dichloride (5) with magnesium as the first isolated P=P compound, was allowed to react with elemental sulfur in triethylamine to give the yellow diphosphene sulfide (3, mp 151.5 - 152°C), which was irradiated or heated in toluene to give 2 almost quantitatively. The intermediate 3 was isolated as a stable compound and was characterized: δ_P 255.8 and 247.8 ppm, J = 629.9 Hz as an AB quartet. 3 was desulfurized with tris(dimethylamino)phosphine to give 4 almost quantitatively while 2 resisted even under severer reaction conditions.

The compounds 2, 3, and 4 were analyzed by X-ray crystallography, for which we are indebted to Dr. Ken Hirotsu and Prof. Taiichi Higuchi at Osaka City University, Japan.