

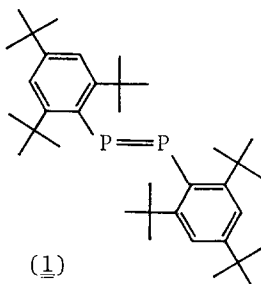
REACTION OF A DIPHOSPHENE WITH VARIOUS HALOGENS

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**SUMMARY** Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene reacts with various halogens to give the corresponding phosphonic dihalides, haloarene, and arene depending upon the halogen and solvent used.

Phosphorus compounds in lower coordination states, particularly those with phosphorus-phosphorus double bond, have been of current interest.<sup>1-6</sup>

We now report our preliminary results<sup>7</sup> on the reaction of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (1)<sup>1a</sup> with various halogens such as chlorine, bromine, and iodine.



The reaction products were straightforward and more interestingly they were depending on the halogen and solvent employed for the reactions as summarized in Table.

Into a solution of 1 (20.5 mg, 0.0371 mmol) in carbon tetrachloride (6 ml) was bubbled through an excess of chlorine gas at room temperature resulting 2,4,6-tri-*tert*-butylphenylphosphonic dichloride (2a) almost quantitatively after the usual workups [2a: mp 96 - 96.5 °C; <sup>31</sup>P NMR (CCl<sub>4</sub>) δ<sub>P</sub> 28.9 ppm; <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 7.37 (d, J = 7.2 Hz, 2H, arom.), 1.54 (s, 18H, o-Bu<sup>t</sup>), 1.33 (s, 9H, p-Bu<sup>t</sup>); IR (KBr) ν<sub>PO</sub> 1260 cm<sup>-1</sup>; MS m/e 362 (M<sup>+</sup>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 160.6 (d, J = 12.2 Hz, o-arom.), 154.9 (d, J = 5.5 Hz, p-arom.), 128.6 (d, J = 159.3 Hz, ipso-arom.), 125.0 (d, J = 20.2 Hz, m-arom.), 41.3 (d, J = 4.9 Hz, o-CMe<sub>3</sub>), 34.8 (d, J = 1.8 Hz, p-CMe<sub>3</sub>), 33.6 (s, o-CMe<sub>3</sub>), 30.8 (s, p-CMe<sub>3</sub>); Anal. (C<sub>18</sub>H<sub>29</sub>POCl<sub>2</sub>) C, H]. The reaction in a mixture of carbon tetrachloride and methanol (v/v 6 : 2) with chlorine gas occurred very similarly to give 2a almost quantitatively.

Table. Reaction Products of 1 with Halogens and Yields of 2, 3, and 4.

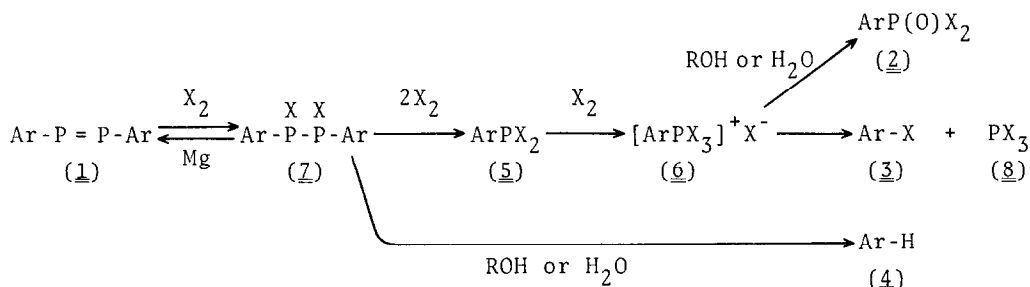
$X_2$	Equiv.	Solv.	ArP(O) $X_2$ ( <u>2</u> )	ArX ( <u>3</u> )	ArH ( <u>4</u> )
Cl <sub>2</sub>	> 4	CCl <sub>4</sub> , MeOH/CCl <sub>4</sub>	~100%	---	---
Br <sub>2</sub>	4	CCl <sub>4</sub>	---	~100%	---
Br <sub>2</sub>	4	MeOH/CCl <sub>4</sub>	~100%	---	---
I <sub>2</sub>	> 1	CCl <sub>4</sub> , MeOH/CCl <sub>4</sub>	---	---	~100%

In carbon tetrachloride, when 1 was allowed to react with 2 equiv. of chlorine the formation of phosphonous dichloride 5a was observed in <sup>31</sup>P NMR spectrum ( $\delta_p$  153.1 ppm). In a separate experiment, chlorine gas was bubbled through into a solution of 5a to give the salts due to 6a ( $\delta_p$  82 ppm in CDCl<sub>3</sub> and 84 ppm in C<sub>6</sub>D<sub>6</sub>), which turned out to be a synthetically useful intermediate for the preparations of the phosphonic dichloride 2a after addition of water and for the corresponding phosphonothioic dichloride, ArP(S)Cl<sub>2</sub>, after adding hydrogen sulfide<sup>8</sup> [mp 148.5 - 149 °C; <sup>31</sup>P NMR (CDCl<sub>3</sub>) 81.1 ppm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.30 (d, J = 7.9 Hz, 2H, arom.), 1.58 (s, 18H, o-Bu<sup>t</sup>), 1.32 (s, 9H, p-Bu<sup>t</sup>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  159.2 (d, J = 11.6 Hz, o-arom.), 153.6 (d, J = 5.5 Hz, p-arom.), 134.6 (d, J = 117.2 Hz, ipso-arom.), 124.6 (d, J = 18.3 Hz, m-arom.), 42.2 (d, J = 4.9 Hz, o-CMe<sub>3</sub>), 34.6 (d, J = 2.5 Hz, p-CMe<sub>3</sub>), 34.3 (d, J = 1.2 Hz, o-CMe<sub>3</sub>), 30.9 (d, J = 1.2 Hz, p-CMe<sub>3</sub>); Anal. (C<sub>18</sub>H<sub>29</sub>PSCl<sub>2</sub>) C, H].

The reaction of 1 with 4 equiv. of bromine was of much interest because the products depended upon the solvent used. In carbon tetrachloride, the reaction product was 2,4,6-tri-tert-butylbromobenzene (3b) in almost quantitative yield, whereas the product in methanol - carbon tetrachloride was the phosphonic dibromide 2b [mp 103.5 - 105 °C; <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta_p$  -1.8 ppm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.35 (d, J = 8.6 Hz, 2H, arom.), 1.58 (s, 18H, o-Bu<sup>t</sup>), 1.31 (s, 9H, p-Bu<sup>t</sup>); MS m/e 450 (M<sup>+</sup>)] almost quantitatively. When 2 equiv. of bromine was used in carbon tetrachloride, a mixture of 3b and 1,3,5-tri-tert-butylbenzene (4) was obtained (ca. 2 : 1), whereas in a mixture of methanol and carbon tetrachloride the reaction with 2 equiv. of bromine gave 2b in only 25% yield after chromatography.

The reaction of 1 with iodine (4 equiv.) gave 1,3,5-tri-tert-butylbenzene (4) both in carbon tetrachloride and in a mixture of methanol and carbon tetrachloride almost quantitatively. The reaction with iodine proceeded with one equiv. of iodine to give 4 in almost quantitative yield after the usual workups.

The mechanisms of these reactions of the diphosphene 1 with various halogens have not been clear so far, however, it could be considerable that in the



Ar = 2,4,6-Bu<sup>t</sup><sub>3</sub>C<sub>6</sub>H<sub>2</sub>; R = Me

a: X = Cl, b: X = Br, c: X = I

cases of excess chlorine and bromine, the reaction occurs at first to give 5 via 7 and then to give 6 as a common intermediate, and the following step affording 2 or 3 depends on the kinds of halogens or solvents. Actually it has been proved that 5a reacts with chlorine to give 6a and in the case of bromine the formation of the bromide (8b) was observed in <sup>31</sup>P NMR during the reaction. The reaction of 6b to 3b or 2b seems very fast at room temperature since the diphosphene 1 in benzene immediately reacted with 2.4 equiv. of pyridinium tribromide (C<sub>5</sub>H<sub>5</sub>N<sup>+</sup>H·Br<sub>3</sub><sup>-</sup>), without giving <sup>31</sup>P NMR signals due to 6b or 5b, we observed signals due to 8b at δ<sub>p</sub> 227.8 ppm and at 72.8 ppm probably due to 7b resulting 4 during the workup procedure, which agreed well with the experimental results. Methanol could promote an intramolecular Michaelis-Arbusov reaction<sup>9</sup> toward 6 to give 2 as mentioned above. In the case of iodine, the iodine atom seems too large to form 6c or even 5c and an alternative intermediate such as 7c is plausible which could be hydrolyzed to give 4. In fact, in carbon tetrachloride, 1 was allowed to react with one equiv. of iodine and we observed a signal at δ<sub>p</sub> 72.2 ppm in <sup>31</sup>P NMR and those in <sup>1</sup>H NMR at δ 7.4 - 7.2 (m, 2H, arom.), 1.63 (s, 18H, o-Bu<sup>t</sup>), and 1.40 (s, 9H, p-Bu<sup>t</sup>), which might be assignable to 7c, and on adding water to it, 4 was obtained almost quantitatively according to the <sup>1</sup>H NMR spectrum of the reaction mixture [4: δ 7.10 (s, 3H, arom.) and 1.30 (s, 27H, Bu<sup>t</sup>)]; 7c appeared at δ<sub>p</sub> 73.0 ppm in THF and on adding magnesium turnings it again gave the starting diphosphene 1 (δ<sub>p</sub> 492.3 ppm).

Further mechanistic studies on these reactions are in progress now.

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## References and Notes

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