

bromo diketones; one is much more reactive than the other, and has been compared with a previously known structural isomer.

4. In all reactions in which the cyclopropane ring is attacked it is opened in the position in which it was closed, the 1,2-position, regardless of the nature of the reagent. This regularity is in marked contrast to the results found by previous investigators in cyclopropane chemistry.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF VICTOR CHEMICAL WORKS]

### SULFUR ADDITION WITH THE AID OF THIOPHOSPHORYL CHLORIDE AND THE CATALYSIS OF TRIARYL THIOPHOSPHATE FORMATION

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Up to the present, thiophosphoryl chloride has not been used as a source of sulfur for the addition of sulfur to organic compounds. Some observations of this type of reaction of thiophosphoryl chloride were made and are described below.

Thiophosphoryl chloride changed triphenyl phosphite into triphenyl thiophosphate, tri-*o*-cresyl phosphite into tri-*o*-cresyl thiophosphate and diphenylmonochlorophosphite into diphenylmonochloro thiophosphate. The method of preparation consisted in mixing equimolecular amounts of organic phosphite and thiophosphoryl chloride, warming the mixture until reaction occurred, which was very violent at the start. It was completed by refluxing and the products were isolated by fractional distillation.

Phosphorus trichloride distilled over first. Then the thiophosphate formed was distilled *in vacuo*. This transfer of sulfur from the thiophosphoryl chloride to the organic phosphite proceeds without side oxidations. The thiophosphate is colorless. Sulfur additions to organic phosphites have been carried out previously by heating organic phosphites with flowers of sulfur.<sup>1</sup> However, in this latter method yellowish-colored side products are formed, which are not readily separated from the thiophosphate.

The addition of sulfur with the aid of thiophosphoryl chloride, as described above, affords an explanation for an interesting catalysis in thiophosphate formation. If pure thiophosphoryl chloride, rectified by distillation, is refluxed with a phenol, only little triaryl thiophosphate may be obtained. The addition of small amounts of phosphorus trichloride catalyzes the reaction in a high degree. When 3 moles of phenol are refluxed with 1 mole of very pure thiophosphoryl chloride, one obtains after seven

<sup>1</sup> (a) Anschütz and Emery, *Ann.*, **253**, 117, 118 (1889); (b) Walter Broeker, *J. prakt. Chem.*, [2] **118**, 287-294 (1928).

hours only a 16% yield of triphenyl thiophosphate. If on the other hand the experiment is carried out under the same conditions with the sole exception that 1.8% (by weight) of phosphorus trichloride is added to the thiophosphoryl chloride, the yield of triphenyl thiophosphate is 99.5%. The very plausible explanation of this catalysis is that triphenyl phosphite is formed first from the phenol and the small amounts of phosphorus trichloride present and that to this phosphite the thiophosphoryl chloride gives off its sulfur, regenerating phosphorus trichloride.<sup>2</sup>

In the sulfur additions with thiophosphoryl chloride the phosphorus-sulfur linkage is broken and the sulfur migrates. The alternative explanation would be the assumption of migrating phenoxy groups. To disprove the latter explanation, it was shown that phosphenyl chloride and thiophosphoryl chloride react with each other when refluxed, yielding phosphorus trichloride and phosphenyl thiochloride. This compound has been formed previously by the addition of elementary sulfur to phosphenyl chloride,<sup>3</sup> and by the reaction of sulfur monochloride with phosphenyl chloride.<sup>4</sup> In this case sulfur migration is the only assumption which may explain the outcome of the experiment, since the carbon-phosphorus linkage is certainly kept unchanged under the mild conditions of refluxing the two liquids. H. Köhler<sup>4</sup> has already remarked that the sulfur has a greater affinity for the phosphorus in phosphenyl chloride than for the phosphorus in phosphorus trichloride, since sulfur monochloride reacts violently with the former, but does not react with the latter, unless heated under pressure. Of this greater affinity the reaction of thiophosphoryl chloride with phosphenyl chloride is further evidence.

### Experimental Part

**Triphenyl Phosphite.**—This compound was obtained in particularly pure form and crystallized. No melting point has been reported in the literature, the triphenyl phosphite being described as a liquid. One mole of phosphorus trichloride and three moles of phenol reacted in an all-glass reflux apparatus. The temperature during the reaction did not exceed 205°. The product was rectified twice in a Claisen flask with a very high neck to avoid any contact of the high boiling liquid with stoppers. The product boiled at 209–210° at 1 mm. and crystallized readily when cooled in an ice-salt mixture. The melting point was +17° to 22°.

*Anal.* Calcd. for  $(C_6H_5O)_3P$ : P, 10.1. Found: P, 10.2.

**Triphenyl Thiophosphate.**—One gram mole of triphenyl phosphite was mixed with one gram mole of thiophosphoryl chloride at room temperature in a flask connected with a coil condenser. The mixture was cautiously heated to 55°. A violent reaction

<sup>2</sup> It should be mentioned that other substances like sulfomono-chloride, amines and in particular thionyl chloride and ferrous chloride have been found to exert some catalytic action in the formation of triaryl thiophosphates from phenols and thiophosphoryl chloride.

<sup>3</sup> H. Köhler and A. Michaelis, *Ber.*, **9**, 1053 (1876).

<sup>4</sup> H. Köhler, *ibid.*, **13**, 463 (1880).

ensued, during which phosphorus trichloride was liberated and caught in a receiver joined to the coil condenser; 116 g. of phosphorus trichloride was obtained. The temperature was raised to 160° to complete the reaction and to expel the phosphorus trichloride. Then the mass was subjected to fractional distillation *in vacuo*. The fraction distilling at 230–240° at 1 mm. (the bulk came over at 232°) solidified at 48° and was practically pure triphenyl thiophosphate, 225 g. (65% yield).

**Tri-*o*-Cresyl Thiophosphate.**—35.2 Grams of rectified tri-*o*-cresyl phosphite was mixed with 16.3 g. of thiophosphoryl chloride. The experiment was carried out as in the preceding case of the phenol derivative; 11 g. of phosphorus trichloride was caught and determined as such. The fraction distilling at 260–265° at 1 mm. solidified after eighteen hours' standing at 0°. Its melting point was 45°. It was pure tri-*o*-cresyl thiophosphate. The preparation was mixed with tri-*o*-cresyl thiophosphate prepared from thiophosphoryl chloride and *o*-cresol. The melting point of the mixture was 44.8°.

**Diphenylmonochloro Thiophosphate.**—Thirty grams of diphenyl monochlorophosphite (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>PCl (b. p. 165–174° at 1 mm.) was mixed with 16 g. of thiophosphoryl chloride and refluxed for one hour. In the subsequent fractional distillation, 10 g. of phosphorus trichloride was obtained. At 180–183° at 1 mm., 22 g. of diphenylmonochloro thiophosphate came over. It melted at 64°.

**Phosphenyl Thioclchloride (C<sub>6</sub>H<sub>5</sub>PSCl<sub>2</sub>).**—Equimolecular amounts of thiophosphoryl chloride and rectified phosphenyl chloride (twice distilled *in vacuo* to purify from phosphorus) were heated to 115°. At this temperature reaction set in. It was completed by boiling gently for three hours. The product was then subjected to fractional distillation. Phosphorus trichloride came over first. The remaining compound was subjected to vacuum distillation. At 150° (26 mm.) a colorless oil came over, which had an aromatic odor. The heavy oil was fairly stable to water and had all the properties of phosphenyl thioclchloride.

*Anal.* Calcd. for C<sub>6</sub>H<sub>5</sub>PSCl<sub>2</sub>: S, 15.1; P, 14.7. Found: S, 15.0; P, 14.4.

**The Catalytic Effect of Phosphorus Trichloride on the Formation of Thiophosphates.**—141 Grams of phenol and 84.5 g. of thiophosphoryl chloride were refluxed in an all-glass apparatus. The thiophosphoryl chloride employed was pure, having been rectified through a column; it boiled at 122.6–124.2° (740.6 mm.). The liberated hydrochloric acid gas was titrated. After three hours only 7.8% of the theoretical amount of hydrochloric acid to be expected in triphenyl thiophosphate formation had come over, after thirty hours, only 35% hydrochloric acid. In another experiment carried out under precisely the same conditions, 1 cc. of phosphorus trichloride (0.68% of total reaction mass or 1.8% of the weight of thiophosphoryl chloride employed) was added. After three hours 41% of the hydrochloric acid had come over and after seven hours of refluxing, 99.5%. The reaction was complete.

### Summary

Some organic phosphorus derivatives containing trivalent phosphorus are capable of being oxidized by thiophosphoryl chloride.

Small amounts of phosphorus trichloride catalyze the formation of triaryl thiophosphates from phenols and thiophosphoryl chloride.

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