

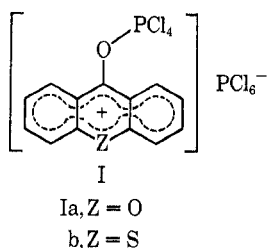
Ion-Pair Complexes of Phosphorus Pentachloride with Xanthone and Thioxanthone

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In 1965 Slater and Wendler¹ reported the conversion of 5*H*-dibenzo[*a,d*]-10,11-hydrocyclohepten-5-one to its 10,11-dihydro derivative. They postulated the dibenzotropylium cation-chloride anion as the red crystalline intermediate. In this laboratory we have isolated from xanthone and thioxanthone reactions with phosphorus pentachloride a yellow crystalline solid and a red crystalline solid, respectively. Our data agree with the cation structure as suggested by Slater and Wendler, but our experimental results indicate the anion is not the chloride ion but the hexachlorophosphate anion as depicted in I.



Phosphorus pentachloride is known to exist in the solid state as ion pairs of tetrachlorophosphonium cation (PCl_4^+) and hexachlorophosphate anion (PCl_6^-).² In solvents of high dielectric constant, phosphorus pentachloride is shown to dissociate into ion pairs by transport experiments.³ Consequently, the presence of the hexachlorophosphate anion in the xanthone and thioxanthone complexes was not unexpected. The results do question, however, the intermediate postulated (but not isolated or identified) by Slater and Wendler.¹

The xanthone and thioxanthone complexes were generated in both toluene containing phosphoryl chloride and methylene chloride containing no phosphoryl chloride. In each solvent system the molecular complexes proved to be identical.

Evidence to support the cation I was the infrared spectra of the complex ions which revealed the loss of the carbonyl stretching frequency. Gravimetric analysis for the xanthone and thioxanthone content plus the potentiometric chloride ion titration of the hydrolyzed products established the identity of the molecular complexes.

An attempt to obtain nmr spectral data for hydrogen for the complexes was not successful. The solvents deuterated chloroform, hexachloroacetone, hexachlorobutadiene, phosphoryl chloride, and methylene chloride could not be used because of slight solubility of the complexes. A variable temperature probe was available on the nmr R-20 instrument, but decomposition of the complexes occurred at elevated temperatures.

Cook⁴ has studied Lewis acid complexes of xanthone

and correlated their carbonyl stretching frequency shift with the strength of the Lewis acid. His study included over 20 inorganic Lewis acids but phosphorus pentachloride was noticeably absent.

Aliphatic ketones react with phosphorus pentachloride to produce *gem*-dichloro compounds and chlorinated olefins.⁵⁻⁹ Aromatic ketones, as a general rule, are unreactive to phosphorus pentachloride. Benzophenone¹⁰ and fluorenone¹¹ are exceptions to this rule and have been successfully converted to *gem*-dichloro compounds. Xanthone and thioxanthone react but do not form the *gem*-dichloride. The reason they do react and form the ion-pair complexes (I) may be explained by the aromatic character of the cation which is similar to the tropylium ion of Wendler and Slater.¹ For this to occur, a nonbonding pair of electrons from oxygen to sulfur (the heteroatoms in the ring) becomes delocalized over the benzene ring structures to comply with the Huckel $4n + 2$ rule (14 π electrons) (see I).

Fluorenone reacts to form the 9,9-dichlorofluorene product for two reasons: the intermediate tetrachlorophosphoniumfluorenone adduct is not stabilized by the aromatic character of the cation (12 π electrons) and some of the strain in the five-membered ring is relieved by the conversion of the nine-carbon atom from an sp^2 to an sp^3 configuration. The reactivity of fluorenone toward phosphorus pentachloride can be decreased by electron-withdrawing substituents. The 2,4,7-trinitrofluorenone would not react with phosphorus pentachloride in either toluene (containing 0.145 *M* phosphoryl chloride) at 100° or refluxing methylene chloride. Undoubtedly, the electron density on the oxygen had been reduced to such an extent that tetrachlorophosphonium ion would no longer form the intermediate cation adduct.

Experimental Section

Xanthone $\text{PCl}_4^+-\text{PCl}_6^-$.—To a solution of dry toluene (60 ml) were added 15 g (0.098 mol) of phosphoryl chloride, 49 g (0.28 mol) of xanthone, and 87.5 g (0.42 mol) of doubly sublimed phosphorus pentachloride. The solution, protected with a drying tube, was heated on a steam bath for 6 hr and a large amount of a bright yellow precipitate formed. The reaction mixture was rotary evaporated to dryness, and the distillate was checked by vpc for any decrease in the phosphoryl chloride concentration. Calibration curves of phosphoryl chloride solutions in toluene indicated the amount recovered was greater than 97%. The yellow residue reacted with water and/or ethanol to regenerate xanthone. Several recrystallization attempts of the yellow residue resulted in decomposition of the ionic complex. A successful purification was accomplished by adding 3.8 g (0.194 mol) of xanthone in 50 ml of methylene chloride to 4.0 g (0.194 mol) of doubly sublimed phosphorus pentachloride in 50 ml of methylene chloride. (All of the filtrations, weighings, and manipulations were carried out in a drybox). The solution was filtered after setting 24 hr at room temperature and washed with anhydrous ether. The crystals (64.7 mg, 0.4% yield) were dried in a drying pistol for 8 hr at 40°, mp 243–244° dec. Samples (2–5 mg) of the ionic salt were hydrolyzed with hot water for 24 hr. Equivalent weights

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were determined by titrating the chloride ion with standardized silver nitrate (0.0100 *N*) solution to a Mohr visual end point.

Anal. Calcd for $C_{13}H_9O_2P_2Cl_{10}$ (equiv wt): 61.27. Found: 61 ± 0.5 (average and average deviation for four determinations).

Gravimetric analysis for the per cent of xanthone in the complex was carried out by hydrolyzing the samples (160–200 mg) at room temperature for 24 hr. The xanthone was collected on weighed filter paper and dried in a drying pistol for 24 hr by using continuous vacuum without applying heat. Phosphorus pentoxide was the desiccant used in the drying pistol. Three samples were run varying in weight from 168 to 200 mg.

Anal. Calcd for xanthone (wt %): 32.02. Found: 34.3 ± 2.3 (average and average deviation for three determinations).

A large scale reaction was run in methylene chloride to check for any phosphoryl chloride. A 10-g (0.051 mol) sample of xanthone was added to 100 ml of methylene chloride containing 10.6 g (0.051 mol) of phosphorus pentachloride. The solution was rotary evaporated, and the distillate was checked by vpc for phosphoryl chloride. None was present.

Thioxanthone $PCl_4^+-PCl_6^-$.—The same procedures as described above for xanthone were followed with thioxanthone. Thioxanthone (Aldrich Chemical Co.) was recrystallized once from toluene, mp 208–209°. The quantities used were 10 g (0.047 mol) of thioxanthone, 41.8 g (0.071 mol) of phosphorus pentachloride, and 22.2 g (0.145 mol) of phosphoryl chloride in 100 ml of dry toluene. During the 3-hr reflux period, a bright red precipitate formed. Gas chromatographic analysis revealed no change in the phosphoryl chloride concentration. Similar results were observed when 8.6 g (0.0405 mol) of thioxanthone and 8.4 g (0.0405 mol) of phosphorus pentachloride in 200 ml of dry methylene chloride were stirred for 20 hr at room temperature. Again, no phosphoryl chloride was generated.

The pure ionic complex was generated by mixing a solution of 1.72 g (0.0081 mol) of thioxanthone in 100 ml of methylene chloride with a 100-ml solution of 1.65 g (0.0081 mol) of phosphorus pentachloride. The solution was filtered after 24 hr, washed with methylene chloride, and dried, mp 231–232° dec. Sample sizes for the chloride ion titration varied from 2 to 3 mg and for the gravimetric analysis from 150 to 300 mg.

Anal. Calcd for $C_{13}H_9OSP_2Cl_{10}$ (equiv wt): 62.87. Found: 63 ± 0.0 (average and average deviation for three determinations).

Anal. Calcd for thioxanthone (wt %): 33.67. Found: 35.4 ± 1.5 (average and average deviation for two determinations).

Both of the ionic complexes were extremely hygroscopic. Several unsuccessful attempts were made to obtain carbon, hydrogen, and phosphorus analyses. However, the analytical laboratory was not able to weigh the samples without hydrolysis occurring.

Vpc Analysis.—Standard solutions of phosphoryl chloride in toluene were prepared and analyzed on a Beckman GC-2A gas chromatograph equipped with a thermal conductivity detector and Honeywell 1-mV recorder. The packing contained a 60–60 mesh diatomaceous earth (Gas Pack PA) coated with 15% DC-710 silicon fluid. Isothermal determinations were made at 100° for toluene and 130° for methylene chloride.

Registry No.—Ia, 26219-78-3; Ib, 26219-79-4.

Oxidation of Mercaptans with Diethyl Azodicarboxylate and Trivalent Phosphorus Compounds

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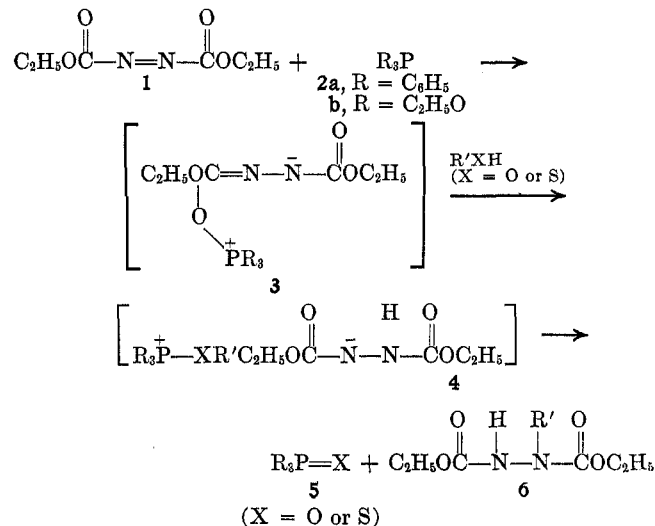
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Schenck, *et al.*,¹ and Cookson, *et al.*,² have reported photochemical dehydrogenation with diethyl azodi-

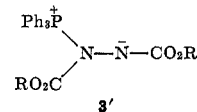
carboxylate (1). Recently, Yoneda, *et al.*,³ have successfully used 1 in a nonphotochemical hydrogen abstracting oxidation of hydrogen donors such as alcohols, mercaptans, or amines. They have found that the reaction of mercaptans with 1 giving disulfides and diethyl hydrazodicarboxylate (7) proceeded under a mild condition; either 1 and the mercaptans were kept without solvent in the dark at room temperature for 1–3 days or the mercaptans and 1 were refluxed in an anhydrous solvent for 0.5–10 hr.

We have investigated the oxidation of trivalent phosphorus compounds (2) using 1 and an alcohol such as benzyl or allyl alcohol and obtained corresponding diethyl *N*-alkyl hydrazodicarboxylates (6) and phosphates or phosphine oxides (5, X = O).⁴ The reaction was explained by assuming the formation of an imidoil phosphonium salt (3),⁵ followed by the nucleophilic attack of the alcohol giving an alkoxy phosphonium salt (4). Since aldehydes and diethyl hydrazodicarboxylate were not produced, the formation of 3 may be faster than the hydrogen abstracting reaction of the alcohol with 1.



In this paper, the possibility that the reaction of mercaptans with 1 and triphenylphosphine (2a) could yield 6 and triphenylphosphine sulfide (5, R = C_6H_5 ; X = S) was investigated. Contrary to our expectation, di-*n*-propyl disulfide and 7 were formed when 1 and 2a were treated with an equimolar amount of *n*-propyl mercaptan at room temperature. Triphenyl-

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