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Reaction of Aromatic Alcohols with Phosphorous Pentasulfide

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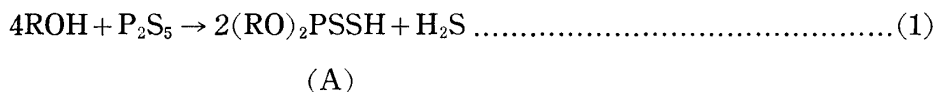
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Synopsis

The reaction of aromatic alcohols and phosphorous pentasulfide has been studied. Primary alcohols and some of the secondary alcohols bearing aryl and alkyl groups yielded O, O-dialkyl hydrogen phosphorodithioates as primary product and these acid esters decomposed easily by heat to give hydrogen sulfide, mercaptans, thioethers and unsaturated hydrocarbons. While the secondary alcohols containing only aryl groups and tertiary alcohols gave only unsaturated hydrocarbons.

I. Introduction

Although considerable attention has been devoted to the reaction between phosphorous pentasulfide and aliphatic alcohols or phenols, the reaction with aromatic alcohols has been largely ignored. As was mentioned by Pistschimuka⁽¹⁾, when aliphatic alcohols or phenols were subjected to the reaction with phosphorous pentasulfide, O, O-dialkyl or diaryl hydrogen phosphorodithioates (A) were obtained as the primary product and mercaptans or unsaturated compounds were given as thermal decomposition products of the acid esters (A). The chemical constitution of the acid esters (I) and the reaction equation were established by Mastin et al.⁽²⁾ as follows:



Engler⁽³⁾ obtained diphenylmethylmercaptan as the product of the reaction between phosphorous pentasulfide and benzhydrol but the formation of the corresponding hydrogen phosphorodithioate (A) was not reported in his literature. The only example of the dialkyl hydrogen phosphorodithioates were diphenoxyalkyl hydrogen phosphorodithioates, reported by Cook and Thomas.^(4a,b)

The purpose of the present work was to determine whether the knowledge obtained by the reaction of aliphatic alcohols with phosphorous pentasulfide could be applied to the reaction with aromatic alcohols.

The 120th report of the Research Institute of Mineral Dressing and Metallurgy. The original of this report written in Japanese, was previously published in *Nippon Kagaku Zasshi* **78** (1957), 236.

(1) P. A. Pistschimuka, *J. pr. Chem.* **84**, (1957), 748.

(2) T. W. Mastin et al., *J. Am. Chem. Soc.* **67** (1954), 1662.

(3) C. Engler, *Ber.* **11** (1878), 925.

(4) E. Cook, Wm. D. Thomas, a) U.S. 2,344, 395, *Chem. Abst.* **38** (1544), 3829 ;
b) U.S. 2,382,775, *Chem. Abst.* **39** (194), 5472.

II. Experimental Results

The following nine alcohols were preferred for the reactions: they were benzyl alcohol $C_6H_5CH_2OH$ (I) and 2-phenylethanol $C_6H_4CH_2CH_2OH$ (II) as primary alcohols, benzhydrol $C_6H_5CHOHCH_5$ (III), α -naphthylphenylcarbinol $C_{10}H_7CHOHC_6H_5$ (IV), 1-phenylethanol $C_6H_5CHOHCH_3$ (V) and ethylphenylcarbinol $C_6H_5CHOHC_2H_5$ (VI) as secondary alcohols, and triphenylcarbinol $(C_6H_5)_3COH$ (VII), tri-p-tolyl carbinol $(CH_3C_6H_4)_3COH$ (VIII) and dimethylphenyl carbinol $(CH_3)_2C_6H_5OH$ (IX) as tertiary alcohols. As to secondary and tertiary alcohols it should be mentioned that the alcohols (V), (VI) and (IX) bear both aryl and alkyl groups, but the others do only aryl groups.

The reactions were performed in accordance with the equation 1. In the case of aliphatic alcohols, O, O-diaralkyl hydrogen phosphorodithiates (A) were obtained as the primary product from the primary alcohols (I, II, V and VI). These acid esters (A) were decomposed by heat to give hydrogen-sulfide, mercaptans, thioethers and polymeric products whose chemical constitutions were not identified. The other alcohols reacted so vigorously that the separation of intermediate products resulted in failure and final ones were obtained in moderately high yields. In these cases the consumption of phosphorous pentasulfide were so poor that it might be reasonable to assume that the reaction did not proceed by the mechanism in which phosphorous pentasulfide was used to form hydrogen phosphorothioates (A). However, in every case, coloring phenomena which would suggest the formation of free radicals could be observed.

For reason to show the results briefly, the outline of the reactions are shown in Table 1.

In the Table 1, PS means phosphorous pentasulfide.

It is clear from the table that in the case of some alcohols (for instances III and IV) products obtained by the reactions with phosphorous pentasulfide were the same as those with sulfur.⁵⁾ As well known, phosphorous pentasulfide is manufactured by reaction of elemental sulfur with phosphorous. Therefore, phosphorous pentasulfide which was applied in the present work was purified until the content of sulfur could be assumed as negligible to avoid confusion in the result given by impurity of the chemical.

III. Experimental Part

All alcohols except benzyl alcohol were prepared by Grignard reaction and their physical properties indicated high purity. Benzyl alcohol was commercial one but was used after distillation in vacuo. Commercial phosphorous pentasulfide was re-distilled in vacuo and a fraction boiling at 345–348°C/2 mm was collected. The solidified fraction was ground in a porcelain mortar, washed with hot carbon disulfide and dried in a desiccator.

(5) L. Szperl, T. W. Kowalski, Chem. Abst. 11 (1919), 2865.

Table 1. Products of the Reactions between Phosphorous Pentasulfide and Aromatic Alcohols

Alcohols		PS		O, O-Diaralkyl hydrogen phosphorodithioates		Thermal Decomposition	
Alcohols	Applied g	Applied g	Unreacted g	Solvent or temperature °C	Ni salt	Temperature	Products
I	22.0	11.0	tr.	Benzene	mp 137	95<	Hydrogen sulfide, benzyl mercaptan, benzyl sulfide, stilben, polymer.
II	9.8	4.4	tr.	120	mp 84 ^{e)}	160-210	Hydrogen sulfide, phenetyl mercaptan ^{e)} 1.2 g, phenetyl sulfide ^{e)} 2.1 g, styrene ^{f)} 0.8 g, polymer.
III ^{e)}	7.4	2.2	2.0			80<	Diphenylmethyl ether.
III ^{b)}	7.4	2.2	0.3			in toluene	Hydrogen sulfide (tr.), Bis-diphenylmethyl disulfide.
IV	9.4	2.2	2.1			95<	Phenyl-naphthylmethyl ether ^{d)} 4.5 g.
V	9.7	4.4	tr.	Benzene	Oily	85<	Methylmercaptan, α -methylbenzylmercaptan, stilben, hydrogen sulfide, polymer
VI	10.7	4.4	tr.	Benzene	Oily	85<	Ethylmercaptan, ^{b)} α -ethylbenzylmercaptan, ^{b)} stilben, ^{f)} hydrogen sulfide, polymer.
VII	19.5	4.4	4.0			95<	Hydrogen sulfide (tr.), triphenyl carbinol.
VIII	24.4	4.4	4.1			95<	Hydrogen sulfide (tr.), tri-p-tolyl carbinol ^{c)} 13.0 g.
IX	9.6	4.4	4.0			95<	Hydrogen sulfide (tr.), α -methylstilbene ^{b)} e 6.5 g.

a) Coarse particle of phosphorous pentasulfide was used.

b) Fine particle of phosphorous pentasulfide was used.

c) Anal. Calcd. for $C_{32}H_{36}NiO_4P_2S_4$; Ni, 7.36%, Found: Ni, 7.30%.

d) Anal. Calcd. for $C_{16}H_{18}S$; S, 13.23%. Found: S, 13.39%.

e) Identified as phenetyl 2,4-dinitrophenyl sulfide, mp 90°C. Anal.

Calcd. for $C_{14}H_{12}N_2O_4S$; S, 10.68%. Found: S 10.68%.

f) Identified as dibromide.

g) Anal. Calcd. for $C_{34}H_{26}O$; C, 90.66%, H, 5.79%. Found: C 90.81%.

H, 5.77%

h) Anal. Calcd. for $C_{36}H_{44}NiO_4P_2S_4$; Ni, 7.48%. Found: Ni 7.71%.

i) Identified as ethyl 2,4-dinitrophenyl sulfide, mp 114.5°C.

j) Identified as α -ethylbenzyl 2,4-dinitrophenyl sulfide, mp 88.5°C.

Anal. Calcd. for $C_{16}H_{18}O_3P$; P, 15.62%. Found: P, 15.55%.

k) Identified by mixed melting point with the authentic sample.

l) Identified by mixed melting point with the authentic sample.

m) Identified by leading to phosphonic acid ester, mp 95-95.5°C,

Anal. Calcd. for $C_{15}H_{14}N_2O_4S$; S, 10.06%. Found: S, 9.81%.

A typical experiments are described for each type of the alcohols.

1. With benzyl alcohol

a) Preparation of O,O-dibenzyl hydrogen phosphorodithioate and its thermal decomposition products. In a 4-necked flask provided with a thermometer, a reflux condenser, a mechanical stirrer and a dropping funnel was placed 50 cc of benzene and 11 g of phosphorous pentasulfide. A solution of 11 g of benzyl alcohol in 50 cc of dry benzene was added through the dropping funnel while stirring mechanically. The flask was then heated on a steam bath and a reaction with the evolution of hydrogen sulfide was started at near the boiling point of the solvent. The product was divided into 2 parts. A part of it (about 5 cc) was led to a nickel salt of O,O-dibenzyl hydrogen phosphorodithioate of violet crystalline. The recrystallized salt from the mixture of ethyl alcohol and benzene (1 : 1) melted at 137°C.

Anal. Calcd. for $C_{28}H_{28}NiO_4P_2S_4$: Ni, 8.75%.
Found : Ni 8.66%.

The solvent of the other part of the product was removed under reduced pressure on a steam bath at below 60°C, and when the residue (27 g) was heated at near 100°C, a violent reaction with the evolution of hydrogen sulfide was set in and the temperature rose above 180°C. After cooling, the product was extracted with 50 ml of ether and plastical material insoluble in ether was separated by decantation. Ether removed from the ethereal solution and the residue was allowed to stand for one week. Benzil sulfide was filtered and recrystallized from petroleum ether. It melted at 49-50° and mixed melting point with the authentic sample showed no depression.

Anal. Calcd. for $C_{14}H_{14}S$: S, 15.27%
Found : S, 14.91%

The filtrate was subjected to distillation in vacuo under nitrogen atmosphere and a fraction boiling at 104-118°/20 mm was collected. The yield was 2.1 g. This fraction was identified as benzyl mercaptan by leading to its 2, 4-dinitrophenyl thioether. It melted at 129-130°C (from ethyl alcohol) and mixed melting point with the authentic sample showed no depression.

Anal. Calcd. for $C_{13}H_{10}N_2O_4S$: S, 11.04%
Found : S, 11.31%

b) The results of the distillation of O, O-dibenzyl hydrogen phosphorodithioate. O,O-dibenzyl hydrogen phosphorodithioate derived from 22 g of benzyl alcohol and 11 g of phosphorous pentasulfide was distilled and fractions boiling at 190-200° and 128-145°C/2 mm were collected. The former was identified as benzyl mercaptan by leading to 2, 4-dinitrophenyl thioether melting at 130°C and mixed melting point with the authentic sample showed no depression. The latter was solidified on standing and recrystallized from ethyl alcohol. It amounted to 2.6 g and melted at 235-237°. The mixed melting point comparison was identical.

with stilben.

2. With benzhydrol

a) Reaction with coarse grain of phosphorous pentasulfide. 7.4 g of benzhydrol and 2.2 g of coarse grain of phosphorous pentasulfide were placed in a two-necked flask equipped with a thermometer and a reflux condenser. The mixture was heated to 80° with occasional shaking with hand. A vigorous reaction was started and the temperature rose to above 150°. White colour appeared first and then it turned green in the course of the reaction. About 4 g of unreacted phosphorous pentasulfide was removed by filtration and the cooled filtrate was dissolved with a hot mixture of ethyl alcohol and benzene (3 : 1) and kept in a refrigerator for a week. 5.2 g of colorless crystalline melting at 84–87°C was recrystallized from benzene for several times. The yield of diphenylmethylether was 3.1g and melted at 109–110°C. Admixture with an authentic sample did not depressed the melting point.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.14% ; H, 6.28%.

Found : C, 89.16% ; H, 6.33%.

b) Reaction with fine-sized phosphorous pentasulfide. In a mixture of 7.4 g benzhydrol in 10 cc of toluene was added 2.2 g of phosphorous pentasulfide and refluxed for one day. Occasional tests for the formation of O, O-dibenzhydryl hydrogen phosphorodithioate with methanol solution of nickel sulfate resulted in failure. 0.3 g of unreacted phosphorous pentasulfide was removed and the filtrate was treated in accordance with the method described by Engler. Bis-diphenylmethyl disulfide, amounted 1.2 g, was obtained. Pure product melted at 151°C.

Anal. Calcd. for $C_{26}H_{22}S_2$: S, 16.08%.

Found : S, 16.31%.

3. With 1-phenyl carbinol

A mixture of 9.7 g of 1-phenylethanol and 4.4 g of phosphorous pentasulfide in 50cc of benzene was refluxed for 4 hrs. Small amounts of phosphorous pentasulfide which remained unreacted was removed by filtration and potassium carbonate was added to the filtrate. Potassium salt of O, O-diphenylmethane hydrogen phosphorodithioate was obtained with the evolution of carbon dioxide. The salt was identified by leading to violet oily nickel salt.

Anal. Calcd. for $C_{32}H_{36}NiO_4P_2S_4$: Ni, 8.01%.

Found : Ni, 8.19%.

In another experiment, O, O-diphenylmethane hydrogen phosphorodithioate free from the solvent was prepared as described before and was heated at about 85°C and a violent reaction with the evolution of a mixture of hydrogen sulfide and a gaseous product with a pungent odor occurred and the temperature rose to above 200°C. The gaseous product was led to an ice-cold ether, and ethereal

solution was introduced to 2, 4-dinitrophenyl thioether in the presence of pyridine. A crystalline product melting at 128°C (from ethylalcohol) was obtained and it was identified as methyl 2, 4-dinitrophenylthioether by mixing with an authentic sample led from methyl mercaptan. The products in the reaction vessel was dissolved with ether by means of refluxing, and insoluble plastic material was removed by decantation. After condensing the ethereal solution, the residue was kept in a refrigerator for a few days and a crystalline product, amounting to 1.5 g, was obtained. Mixture with an authentic sample of stilben showed no depression. The filtrate was led to 2, 4-dinitrophenyl thioether and a crystalline melting at 110° was obtained.

Anal. Calcd. for $C_{14}H_{12}N_2O_4S$: S, 10.52%.

Found : S, 10.67%.

4. With triphenylcarbinol

19.5 g of triphenylcarbinol and 4.4 g of phosphorous pentasulfide was heated in a vessel described in 2. A vigorous reaction began at about 95°C and the temperature rose to above 160°C. The colour of the product turned violet during the reaction. The product was refluxed with ether and the cooled solution was decanted to separate insoluble materials. The ethereal solution was condensed and the remain was kept in a refrigerator for a week. Triphenylmethane was obtained and identified by mixed melting point with an authentic sample. The yield was 12.0 g and the melting point was 93-93.5°C.