

## PHOSPHINE ADDUCTS OF POLYNITROARYLS

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Phosphines form addition compounds with polynitro aromatic compounds like picric acid, 1,3,5-trinitrobenzene and 2,4-dinitrophenol. Picrates of the alkyl phosphines are obtained in good yield from stoichiometric amounts of picric acid and phosphines, viz. trimethylphosphine, tributylphosphine, phenyldimethylphosphine, triphenylphosphine and tri-*p*-tolylphosphine. The alkylphosphines react instantaneously at room temperature with the deposition of the intensely coloured compounds. Yellow solids which gradually transform into the deep coloured compounds are also obtained when the reaction is carried out at lower temperatures. With the arylphosphines an intermediate yellow solid is not obtained, the reaction is very slow and it is only on long refluxing that dark solid is obtained. Only the alkylphosphines react with the other nitroaryls. From the intensity of the colour and their reactions with acid and alkali the compounds are suggested to be zwitterionic in nature.

## Introduction

While the deoxygenation reaction of the phosphines with the nitroso compounds<sup>1</sup> is well established, the corresponding reaction with the nitro compounds has received very little attention. The only report in this connection is the reaction of triphenylphosphine and *o*-dinitrobenzene which yields the phosphine oxide and an unidentified product.<sup>2</sup> The formation of an unstable 1:1 adduct of triethylphosphine with *o*-dinitrobenzene has also been reported.<sup>3</sup> We have obtained 1:1 addition compounds of alkyl- and arylphosphines with picric acid. Alkylphosphines alone have been found to react with 1,3,5-trinitrobenzene and 2,4-dinitrophenol. The preparation and the reactions of these compounds is being reported here.

## Experimental

**Phosphines.**—The desired phosphines were prepared by the reaction of phosphorus trichloride or a suitable halide with an appropriate Grignard reagent. The alkyl phosphines were purified by precipitation and subsequent decomposition of their silver iodide or carbon disulphide adducts. Pure arylphosphines were obtained by the hydrolysis of their hydrochloride.

**Preparation of Addition Compounds.**—The phosphines so purified were either passed directly into the ethereal solution of the polynitro compound or were transferred into solution maintaining an inert atmosphere.

## I. Compounds with Picric Acid

(a) **Trimethylphosphine.**— $\text{Me}_3\text{P}\cdot\text{AgI}$  (0.31g, 1 mmole) was decomposed and the phosphine passed into an ethereal solution containing picric acid (0.22 g, 1 mmole). The blood red precipitates in 52% yield were allowed to settle and then washed with ether maintaining an inert atmos-

phere throughout the washing. (Calc. for  $(\text{CH}_3)_3\text{P}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ : N, 13.7; C, 35.4; H, 3.93. Found: N, 13.5; C, 35.3; H, 3.95%; m.p. 118°.) When the phosphine was passed into the acid solution cooled to  $-5^\circ$ , yellow crystals in 25% yield were obtained. (Calc. for  $(\text{CH}_3)_3\text{P}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ : N, 13.7%. Found: N, 13.5%; m.p. 76°.) The yellow compound has an IR spectrum different from the red variety and resembles that of ammonium picrate in the 1200–650  $\text{cm}^{-1}$  region. The yellow compound was unstable and changed red on standing or on heating towards melting. The transition was, however, slow at low temperatures. They were both soluble in the polar organic solvents. The red form was stable in moist air and was unchanged in water at ordinary temperature but on warming phosphine was evolved and the solid turned brown and eventually went into solution forming picric acid. On the addition of hydrochloric acid a yellow solution was immediately obtained and on neutralization of the resulting solution with alkali, the red compound was again precipitated. Decomposition to the trimethylphosphine (identified by its IR spectrum) also occurred on boiling with aqueous sodium hydroxide or ethanolic sodium ethoxide. Violent decomposition occurred on heating the compound in a sealed tube.

(b) **Phenyldimethylphosphine.**—The compound was prepared as in (a) and a 45% yield was obtained. There was a very fast transition from the yellow to scarlet red form, which went to completion in spite of intensive cooling. The yellow compound was, however, obtained in 20% yield when the picric acid solution was added dropwise into a solution of the phosphine. (Calc. for  $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{P}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ , red: N, 11.4; C, 45.7; H, 3.8%. Found: N, 11.5; C, 46.64; H, 4.38%; m.p. 77°. Yellow, Found: N, 11.7%; m.p. 115°.) The compound showed similar reactions as the trimethylphosphine analogue

towards water, acid and alkali. Heating decomposed it with explosive violence. The IR spectrum of the yellow compound was different from the red form and in this case also the former resembled one of ammonium picrate.

(c) *Tri-n-butylphosphine*.—Only the yellow compound was obtained in 20% yield on mixing equimolar solutions of tri-n-butylphosphine and picric acid. (Calc. for  $(C_4H_9)_3P \cdot C_6H_2(NO_2)_3OH$ : N, 9.7%. Found: N, 10.0%; m.p. 65°.) The compound was stable at room temperature and decomposition seemed to be very slow since the evolution of phosphine was barely noticeable. On standing for a few days reddish brown syrupy material was left behind. Water and alkali both decomposed the compound and phosphine was evolved during the process. With acid a yellow coloration was obtained when the compound was dissolved. On neutralization of this solution an intensity in its colour was noted. The IR spectrum of this compound was similar to the yellow compounds obtained in the case of (a) and (b).

(d) *Triphenylphosphine*.—The reaction with picric acid did not occur at room temperature by simple mixing. The solution of the mixture was required to be refluxed for 24 hr when orange red crystals started separating and 40% yield was obtained. (Calc. for  $(C_6H_5)_3P \cdot C_6H_2(NO_2)_3OH \cdot 3H_2O$ : N, 8.5; C, 52.8; H, 4.4%. Found: N, 8.5; C, 53.48; H, 3.57%; m.p. 145°.) This compound was comparatively stable towards air and water. Its reactions with hydrochloric acid gave a pale yellow coloration to the solution and when the solution was neutralized the original colour was again obtained. With the alkali solution only slight decomposition occurred and sodium picrate was one of the products. The IR spectrum of this compound resembled the red compounds obtained in (a) and (b).

(e) *Tri-p-tolylphosphine*.—The reaction was very slow at ordinary temperatures. Mixing the solution of the components gave a reddish coloration. Orange crystals were slowly deposited in 30% yield when the mixture was refluxed for 24 hr. (Calc. for  $(CH_3C_6H_4)_3P \cdot C_6H_2(NO_2)_3OH$ : N, 7.8%. Found: N, 7.7%; m.p., 112°.) The reaction of this compound and also its IR spectrum resembled that of its analogue (d).

## II. Compound with 1,3,5-Trinitrobenzene

(a) *Trimethylphosphine*.—The addition compound was obtained by passing trimethylphosphine into a cold ethereal solution of the trinitrobenzene. The precipitation of dark violet solids started on warming to room temperature giving 40% yield. (Calc. for  $(CH_3)_3P \cdot C_6H_3(NO_2)_3, H_2O$ : N, 14.5; C, 35.1; H, 4.56%. Found: N, 14.7; C, 34.26; H, 5.00%; m.p. 110°.) The compound was

stable at room temperature in dry air. On standing in moist air it decomposed into a gummy substance. It was soluble in most of the polar organic solvents and was insoluble in water. On keeping in water for some time the aqueous layer turned brown and phosphine was slowly evolved. With hot water the evolution of the phosphine was rapid. With hydrochloric acid the complex dissolved giving a pale yellow color. The solution turned violet again on neutralization with alkali. The compound decomposed giving phosphine as one of the products when boiled with alkali.

(b) *Phenyldimethylphosphine*.—The compound was prepared by mixing equimolar quantities of the phosphine and the trinitrobenzene in ether. After 3 hr the addition compound slowly precipitated as dark violet crystals in 50% yield. (Calc. for  $C_6H_5(CH_3)_2P \cdot C_6H_3(NO_2)_3$ : N, 12.0; C, 47.8; H, 3.6%. Found: N, 12.2; C, 47.47; H, 3.96%; m.p., 80°.) This compound shows similar behaviour towards acid and alkali as the trimethylphosphine analogue.

(c) *Tri-n-butylphosphine*.—On mixing equimolar ethereal solution of the phosphine and trinitrobenzene an orange coloration developed. This gave a dark brown gummy substance which could not be properly characterized. On treatment of this substance with water and alkali the phosphine was evolved.

(d) *Triphenylphosphine and tri-p-tolylphosphine*.—No addition compound could be isolated in spite of prolonged refluxing in ether.

## III. Compounds with 2,4-Dinitrophenol

(a) *Trimethylphosphine*.—Equimolar quantities of the phosphine and dinitrophenol were allowed to react at room temperature in ether solution. Orange crystals in 45% yield started separating soon after the admixture. (Calc. for  $(CH_3)_3P \cdot C_6H_3(NO_2)_2OH$ : N, 10.8%. Found: N, 11.4%; m.p. 95°.) The compound was soluble in polar organic solvents and was insoluble in water. A yellow colour was slowly imparted to the aqueous layer on standing and phosphine (identified by its IR) was slowly evolved. It dissolved with decomposition in hot water giving phosphine. In an alkaline solution the decomposition was rapid and phosphine evolved rapidly. Pale yellow solution resulted when the compound was treated with hydrochloric acid and an orange coloration was noted when this solution was neutralized with alkali.

(b) *Phenyldimethylphosphine*.—When equimolar solutions of the phosphine and dinitrophenol were mixed a slight amount of yellowish turbidity was immediately noticed. Orange red precipitates were slowly deposited and after 36 hr a 30% yield was obtained. (Calc. for  $C_6H_5(CH_3)_2P \cdot$

$C_6H_3(NO_2)_2OH \cdot H_2O$ : N, 8.8; C, 49.4 H, 5.0%. Found: N, 9.1; C, 49.81; H, 4.32%; m.p., 103°. The reactions of the compound with water, alkali and acid were the same as in section III(a).

(c) *Tri-n-butylphosphine*.—The mixture of equimolar quantities gave 12% yield after 48 hr. The orange red crystals were not stable under ordinary conditions and decomposed easily on standing, giving off phosphine. (Calc. for  $(C_4H_9)_3P \cdot C_6H_3(NO_2)_2OH$ : N, 7.3%. Found: N, 7.8%; m.p. 182°). The other reactions of this compound are similar to III(a).

(d) The ethereal solutions of triphenyl or tri-*p*-tolylphosphine when refluxed with the dinitrophenol did not yield any addition compound.

### Discussion

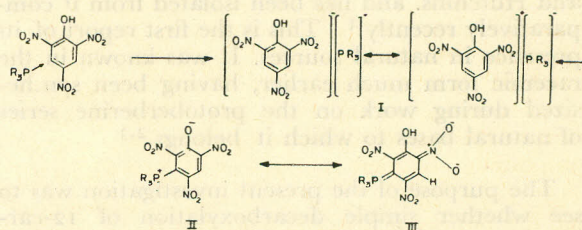
The formation of the addition compounds of phosphine with the polynitro aromatic compounds introduces them to the already long list of substances known as Meisenheimer complexes.<sup>4-6</sup> Some of the main characteristics of these compounds are: (1) the arylphosphines form the picrates with difficulty and give no compounds with 1,3,5-trinitrobenzene or dinitrophenol, (2) trimethyl- and phenyldimethylphosphine form yellow as well as red compounds having similar analytical data, (3) there is a slow transition of the yellow into the dark coloured compounds on standing and (4) the IR spectrum of the yellow compounds are similar to those of the amine picrates.

The instantaneous formation and the deep colour of the addition compounds with the alkyl phosphines and the difficulty in obtaining them from the arylphosphines reminds one of the carbon disulphide and the quinone adducts. This must be attributed to the basicity of these phosphines<sup>7,8</sup> which is responsible for the ease in their quaternization. It is known that highly electronegative phosphines do not react to form addition compounds with boron trifluoride.<sup>9</sup> Apparently the difference in the electronegativity of the donor and the acceptor is too small and hence there is a reluctant transfer or drift of the bonding electron from the former. In picric acid the presence of four electron-withdrawing groups would promote the drift of electrons from the phosphines. In the *s*-trinitrobenzene and 2,4-dinitrophenol, however, such a tendency is reduced, which might be one of the reasons for the nonoccurrence of adducts with these two compounds.

The carbon disulphide and the quinone adducts both have been shown to have a zwitterionic nature.<sup>10,11</sup> A similar structure is quite likely in the present case also. That they are zwitterionic is shown by the reaction with water, alkali and acid. In these reactions they parallel the two

classes of compounds just mentioned. In both cases the corresponding phosphine is one of the products of decomposition. In comparison with the other molecular compounds these substances are more stable. They do not decompose instantaneously and melt without decomposition. Heating above the melting point usually decomposes these compounds with explosive violence. However, the weak binding with the nitroaryl moiety is shown by the decomposition on dissolving in polar solvents and on treatment with water.

From the above discussion it may be suggested that the complexes may either be charge transfer type (I) or may have a fully covalent structure (II).



The yellow compounds isolated in the case of the alkyl phosphines have IR spectra similar to the charge transfer complexes formed by the amines and hydrocarbons.<sup>12</sup> These compounds slowly undergo transformation into a deep coloured variety as observed for trinitroanisole.<sup>5</sup> This has been attributed to the transformation of the charge transfer type complex into the covalent bonded structure. A similar phenomenon must be occurring in the present case. This also supports a zwitterionic structure for the complexes.

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