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Synthesis, Applications and Comparison of Some Phosphine Oxides and Their Salts with the Nitrogen Containing Compounds

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Some phosphine oxides **3, 5** and the corresponding salts **2, 4** have been successfully synthesized as well as nitrogen containing compounds amides **9, 10, 11** and azo-compounds **15, 16, 17**. These synthesized products served as excellent inhibitors in the medium of 15% H_2SO_4 on API 5L 52X steel.

Key Words: Phosphine oxides, Inhibitory.

INTRODUCTION

In recent years, there have been numerous papers describing the synthesis and application of phosphine oxides[1–6]. Recently, the general route for the synthesis and the resolution of racemic phosphine oxides was reported and it was found that the reaction of methyldiphenylphosphine oxide with aldehydes is a convenient synthesis of many phosphine oxides[6, 7]. In this paper, another new application of phosphine oxides and their derivative salts is reported.

EXPERIMENTAL

All 300 MHz ^1H and 75 MHz ^{13}C NMR spectra were run on a Bruker AC 300 NMR spectrometer, 200 MHz NMR spectra were run on a Bruker AC 200 NMR spectrometer. ^{13}C NMR spectra were recorded using distortionless enhancement by polarization transfer. Both ^1H and ^{13}C spectra were recorded using $CHCl_3$ as internal standard. Fast atom bombardment (FAB) was recorded with a Crates MS50 with an *m*-nitrobenzyl alcohol matrix. Accurate mass determinations were carried out on a Kartos Concept IS spectrometer. Elemental analysis was performed using a Carlo-Erba 1106 elemental analyzer. Infrared spectra were recorded using a Perkin-Elmer 783 spectrometer equipped with a PE 600 data station. Melting points were determined using an electrothermal melting point apparatus and were uncorrected.

Column chromatography was conducted using silica gel 230–400 mesh (Merck & Co.). Silica thin layer chromatography (TLC) was conducted on percolated aluminum sheets (60 F254) with a 0.2 mm thickness (Aldrich Chemical Co.).

Potentiometric measurements are achieved with the help of an electrochemical chain, constituted of: (i) Potentiostat-Galvanostat: it permits to impose and to measure the potential and the steady currents in the cathodic and anodic domains. (ii) Hardback microcomputer to the potentiostat-galvanostat that permits to control the electrochemical tests, to trace the different curves and to calculate the electrochemical parameters by the slant of the software Master, and (iii) Electrochemical cell composed of three electrodes: one electrode of reference (electrode to the saturated calomel: ECS), one against electrode and one electrode of work.

The electrode of work is an electrode made of steel with carbon of nuance API 5LX52, of circular shape and 0.78 cm^2 section. Before every electrochemical[8-12] test the surface of the work electrode is polished with an abrasive paper, cleaned with acetone and rinsed with distilled water. The corrosive environment is 15% H_2SO_4. The sweep takes place with a speed of 30 mV/min, of –800 to –300 mVs. The rate of inhibition is measured at concentrations 0, 20, 40, 60, 80, 100 and 120 ppm.

Synthesis of phosphinium salts and phosphine oxides

Preparation of methyltriphenyl phosphonium iodide (2): Triphenylphosphine (40 g, 153 mmol) was added to chloroform (200 mL) in a 500 mL round bottomed 3-necked flask equipped with a reflux condenser, sitted bar and a pressure equalizing dropping funnel. The mixture was heated slowly until it begins to reflux gently. The reaction is exothermic. Care must be taken to ensure that the reaction is not too vigorous, by appropriate cooling. The mixture was refluxed for a further 1 h and left to cool. The mixture was transferred to a single necked flask (500 mL) and the chloroform removed under reduced pressure on a rotavapor to leave colourless oil that crystallized on standing. This can, if required, be recrystallized from propan-2-ol to give pure methyltriphenyl phosphonium iodide, m.p. 180–182°C. The material is sufficiently pure to suit most purposes. IR (KBr, cm^{-1}): 1110 ν(P=O); ^1H ($CDCl_3$): δ 3.1 (3H, d, J_{PH} = 13.0 Hz, CH_3), 7.7 (15H, m, Ar—H); ^{13}C ($CDCl_3$): δ 11.50 (d, J_{PH} = 57.3 Hz, CH_3), 117.78 (C), 118.96 (C), 130.59 (d, J_{PC} = 12.1 Hz, CH), 132.94 (d, J_{PC} = 10.56 Hz, CH), 134.68 (CH); m/z (FAB): 403 [$(M+H)^+$, 4], 278 [$(M+H—I)^+$, 11)], [$(M—I)^+$, 100)], 276 (17), 225 (6), 200 (8), 183 (28); anal. Calcd. for $C_{19}H_{18}IP$: C, 56.4; H, 4.5; P, 7.7; Found: C, 56.0, H, 4.5; P, 7.5%.

Diphenylphosphinoylethyl triethyl phosphonium bromide (4): This salt was prepared in a similar fashion to that described above using $Ph_2P(O)CH_2CH_2PEt_2$ (15.9 g, 50 mmol) and ethyl bromide (5.45 g, 50 mmol). The product was isolated as an off-white solid which was recrystalized from ethyl acetate to give diphenylphosphinoylethyl triethyl phosphonium bromide (13.66 g, 35 mmol, 64.3%) as colourless needles, m.p. 127–129°C. IR (KBr, cm^{-1}): 3060 ν(CH aromatic) and 2970–2810 ν(CH aliphatic), 1270 ν(P=O).

Preparation of methyldiphenylphosphine oxide (3): Methyltriphenylphosphonium iodide (63.0 g, 156 mmol) was placed in a one litre round-bottomed flask equipped with a reflux condenser and a large magnetic stirrer bar. Sodium hydroxide (130 g, 3.25 mol) was added in water (200 mL) and the mixture stirred

vigorously. The mixture was heated on an oil bath until there is strong reflux. Drops of benzene were seen condensing in the condenser and an oily layer appeared on the surface of the mixture. It is essential that the biphasic mixture be vigorously stirred to ensure complete reaction. The reaction mixture was cooled slightly and the condenser was replaced by a still-head azeotropically, the benzene was distilled off from the reaction. When the theoretical volume (in this case 14 mL) of benzene was collected the mixture remaining in the round-bottomed flask was cooled. The mixture was extracted with chloroform (3 × 100 mL). The combined extracts were dried by the addition of magnesium sulfate and filtered. The solvent was evaporated under reduced pressure on a rotavapor to give an off-white solid. Recrystallization from a minimum amount of boiling ethyl acetate gave the phosphine oxide (29.3 g, 136 mmol, 87%) as colourless needles, m.p. 107–109°C (Lit. 107–109°C). $R_f = 0.50$ (chloroform); IR (KBr, cm^{-1}): 1170 ν(P═O); ^1H ($CDCl_3$): δ 2.01 (3H, d, $J_{PH} = 13.0$ Hz, CH_3), 7.43–7.56 (6H, m, Ar—H), 7.69–7.77 (4H, m, Ar—H); ^{13}C ($CDCl_3$): δ 16.54 (d, $J_{PC} = 74.0$ Hz, CH_3), 128.55 (d, $J_{PC} = 67.0$ Hz, CH), 131.68 (CH), 134.04 (d, $J_{PC} = 10.1$ Hz, C); m/z (FAB): 433 [$(2M + H)^+$, 24], 217 [$(M + H)^+$, 100)], 183 (5), 139 (29), 107 (4), 89 (10), 77 (12). Anal. Calcd. for $C_{13}H_{13}OP$: C, 72.2; H, 6.0; P, 14.3; Found: C, 72.1, H, 6.3; P, 14.2%.

$Ph_2P(O)CH_2CH_2P(O)Et_2$ (5): This compound was prepared in a similar fashion to that described above using $Ph_2P(O)CH_2CH_2P^+Et_3Br^-$ **4** (1.1 mmol) and sodium hydroxide (0.4 g). The product was isolated as an off-white solid which was recrystallized from ethyl acetate to give phosphine oxide, $Ph_2P(O)CH_2CH_2P(O)Et_2$ (0.56 g, 1.7 mmol, 65.6%) as colourless needles, m.p. 90–92°C. IR (KBr, cm^{-1}): 3060 ν(CH aromatic) and 2960–2890 ν(CH aliphatic), 1170 ν(P═O).

Synthesis of amides

Acetanilide (9): Aniline (10 g, 0.1 mol) was dissolved in 100 mL of concentrated hydrochloric acid and 250 mL of water contained in a 500 mL beaker. The mixture was cooled to 0°C in an ice-salt bath with vigorous stirring. Acetic anhydride (12.6 mL, 133.3 mmol) was added dropwise for 5 min and then sodium acetate (10.6 g, 77.89 mmol) in 75 mL of water was added in one portion to the solution. Almost immediately after the end of the addition, a precipitate was formed. The reaction was stirred for 15 min after which the acetanilide was filtered off and washed with water. The crude white solid was recrystallized from ethyl acetate to afford colourless needles (90%), m.p. 114–116°C. IR (KBr, cm^{-1}): 3290 ν(NH), 3130–3020 ν(CH aromatic), 2950–2850 ν(CH aliphatic) and 1660 ν(C═O).

N-*o*-Tolylacetamide (10): The compound was prepared in a similar fashion to that described above using *o*-tolydine (11.49 g, 107.3 mmol), acetic anhydride (12.6 mL, 133.28 mmol). The product was isolated as white needles after recrystllization from ethyl acetate (15.4 g, 103.22 mmol, 96%), m.p. 102–103°C. IR (KBr, cm^{-1}): 3290 ν(NH), 3110–3030 ν(CH aromatic), 2960–2890 ν(CH

aliphatic) and 1650 ν(C=O). ^{1}H ($CDCl_3$): δ 1.95 (3H, s, CH_3CO), 2.15 (3H, s, Ar—CH_3), 6.8–7.5 (4H, m, Ar—H), 7.65 (1H, br, NH); ^{13}C ($CDCl_3$): δ 18.2 ($\underline{C}H_3CO$), 24.1 (Ar$\underline{C}H_3$), 124.8 (CH), 125.7 (CH), 125.9(CH), 130.8 (CH), 131.2 (C), 136.1 (C) 169.5 (CO).

N-*o*-Tolylbenzamide (11): This compound was prepared in a similar fashion to that described above using *o*-tolydine (11.49 g, 107.3.3 mmol) and benzoyl chloride (15.48 mL, 133.28 mmol). The product was isolated as colourless needles after recrystallization from ethyl acetate (20.77 g, 94.43 mmol, 95.31%), m.p. 110–112°C. IR (KBr, cm^{-1}): 3290 ν(NH), 3070–3030 ν(CH aromatic), 2960–2890 ν(CH aliphatic) and 1680 ν(C=O); ^{1}H ($CDCl_3$): δ 2.1 (3H, s, CH_3), 7.65 (1H, s, br., NH), 7.35–8.2 (9H, m, Ar—H); ^{13}C ($CDCl_3$) : δ 31.3 (CH_3CO), 127.5 (CH), 128.9 (CH), 129.2 (CH), 129.8 (C), 130.6 (CH), 131.0 (CH), 134.2 (CH), 172.7 (C), 207.9 (CO).

Synthesis of azo-compounds

4-(N, N-dimethylaminophenyl)azobenzene (17): Aniline (9.34 g, 100.47 mmol) and sodium carbonate (5.3 g, 50 mmol) were dissolved in 200 mL of water contained in an 800 mL beaker. The mixture was cooled to 0°C in ice bath and then sodium nitrite (7.4 g, 107.2 mmol) dissolved in 100 mL of water was added while the temperature kept at 5°C with vigorous stirring. Concentrated hydrochloric acid (20 mL) in 20 mL of water was also added. N,N-Dimethyl (12.5 g, 100.47 mmol) in 6 mL of glacial acetic acid was added while the temperature was kept at 10°C. The mixture was stirred for 15 min. and then 75 mL of sodium hydroxide (12%) was added with vigorous stirring. After the end of addition of sodium hydroxide, the mixture was heated to dissolve the solids. 10 g of sodium chloride was added and then cooled to 0°C in an ice-bath. The precipitate was filtered off and washed with water. The crude product was recrystallized from ethyl acetate to yield golden-yellow needles of 4-(N,N-dimethylaminophenyl)azobenzene (18.1 g, 80.3 mmol, 80%); m.p. 115–117°C. IR (KBr, cm^{-1}): 3070–3030 ν(CH, aromatic), 2960–2890 ν(CH, aliphatic), 11600 ν(N=N), 1270–1015 ν(C—N).

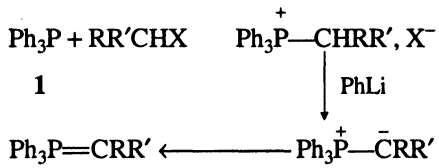
***p*-Tolylazobenzene (15):** This compound was prepared in a similar fashion to that described above using aniline (9.34 g, 100.47 mmol) and toluene (9.24 mL, 100.47 mmol). The product was isolated as red-orange needles after recrystallization from ethyl acetate (13.78 g, 70.42 mmol, 70%), m.p. 113–116°C. IR (KBr, cm^{-1}): 3080–3050 ν(CH aromatic), 2960–2890 ν(CH aliphatic), 1705 ν(N=N) and 1270–1020 ν(C—N).

4-Phenylazoaniline (16): Using a similar method to that described for 4-(N,N-dimethylaminophenyl) azobenzene. After recrystallization from ethyl acetate, the product was obtained as yellow needles of 4-phenylazo aniline (84%), m.p. 121–123°C. IR (KBr, cm^{-1}): 3380–3190 ν(NH), 3080–3050 ν(CH aromatic), 1605 ν(N=N) and 1270–1020 ν(C—N).

RESULTS AND DISCUSSION

Synthesis of phosphonium salts and phosphine oxides

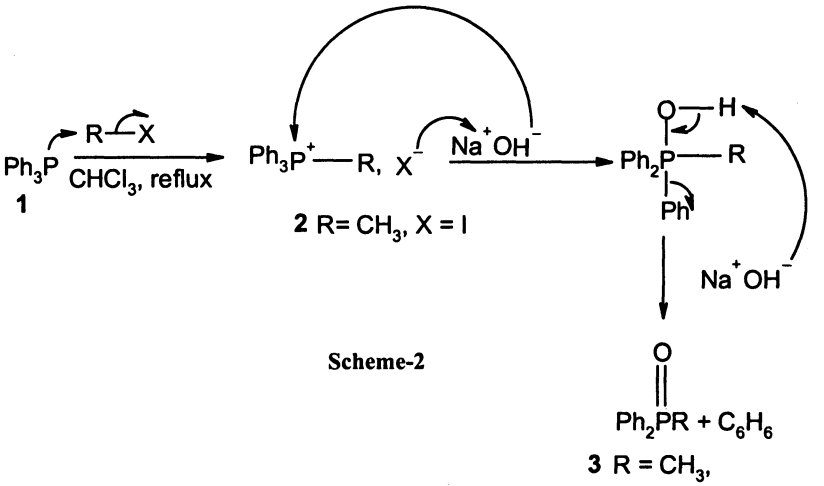
Wittig reaction is an extremely useful reaction for the synthesis of alkenes involving the addition of an alkyl halide, RR'CHX, to triarylphosphine (very often Ph_3P) to yield a phosphonium salt, followed by abstraction of proton from it by strong base, e.g., PhLi **(Scheme-1).**



R and R'=aryl or alkyl.

Scheme-1

However, the synthesis of the phosphonium salt **2** and phosphine oxide **3** from triphenyl phosphine **1** was carried out by modifying the second step of this procedure, which involves adding NaOH to the phosphonium salt **(Scheme-2).**

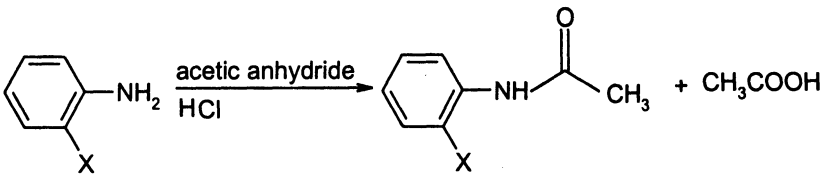


Scheme-2

The salt diphenylphosphinoylethyl triethyl phosphonium bromide $Ph_2P(O)CH_2CH_2PEt_3^+Br^-$ **4** and phosphine oxide $Ph_2P(O)CH_2CH_2P(O)Et_2$ **5** followed the same mechanism as mentioned earlier. Dimethyl phenyl phosphine, Me_2PPh **6**, was prepared in a similar fashion to that described for phosphine oxide using Ph_2PMe and NaH in 63%.

Synthesis of amides

Amides are compounds in which the —OH of the carboxylic acid has been replaced by $—NH_2$. These are generally prepared by the reaction of ammonia with anhydrides like acetic anhydride **(Scheme-3).**



7 X = H
8 X = CH_3

9 X = H
10 X = CH_3

Scheme-3

However, N-*o*-tolylbenzamide was prepared by using benzoyl chloride and was also prepared in a similar fashion to that described above using *o*-tolydine.

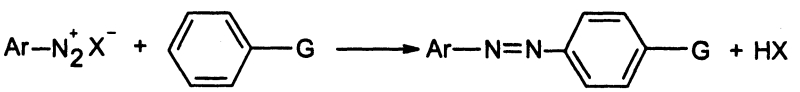
Synthesis of azo-compounds

When a primary aromatic amine, dissolved or substituted in cold aqueous mineral acid, is treated with sodium nitrite, there is formed a diazonium salt **(Scheme-4).**

$$Ar—NH_2 + NaNO_2 + 2HX \xrightarrow{\text{cold}} Ar—N_2^+X^- + NaX + 2H_2O$$

Scheme-4

Since diazonium salts slowly decompose even at ice-bath temperatures, the solution is used immediately after preparation. The diazonium coupled, in which the nitrogen is retained in the product as shown in **Scheme-5.**



12 Ar = Phenyl
13 Ar = Phenyl
14 Ar = Phenyl

15 Ar = Phenyl G = NH_2
16 Ar = Phenyl G = CH_3
17 Ar = Phenyl G = $N(CH_3)_2$

Scheme-5

G must be a strongly electron-releasing group: —OH, NR_2, —NHR, —NH_2.

Survey of the inhibitory efficiency of phosphorus and azo-compounds in 15% H_2SO_4 on API 5L 52X steel: The efficiency of a corrosion inhibitor is defined by its rate of inhibition or percentage of inhibition:

$$\% \text{ d' inhibition} = 100 \cdot \frac{V - V_1}{V}$$

where V_1 is speed of corrosion without inhibitor of corrosion, V is speed of corrosion with inhibitor of corrosion. The rate of inhibition is determined from speeds of corrosion in presence and in absence of inhibitor. Speeds of corrosion are determined by the potentiometric method (Table-1).

Influence of the concentration on the rate of compounds amides inhibition

The best output for the family of compounds amides on steel with carbon of nuance API 5LX52 in 15% H_2SO_4 is obtained for the compound **11** with a concentration of 100 ppm with a rate of inhibition that reaches 97.95% (Table-1).

TABLE-1
EVOLUTION OF THE SPEED OF CORROSION AND THE RATE OF INHIBITION ACCORDING TO THE CONCENTRATION OF COMPOUNDS AMIDES

C (ppm)	9		10		11	
	V_{corr} (mm/year)	R (%)	V_{corr} (mm/year)	R (%)	V_{corr} (mm/year)	R (%)
20	6.016	51.94	5.110	59.18	3.960	68.37
40	5.727	54.25	3.662	70.75	2.366	81.10
60	3.279	73.81	2.698	78.45	1.784	85.75
80	2.284	81.75	2.196	82.46	1.034	91.74
100	0.985	92.13	0.440	96.48	0.256	97.95
120	1.308	89.55	2.290	81.71	2.241	82.10

Influence of the concentration on the rate of azo-compounds inhibition

The best output for the family of azo-compounds in the same conditions is obtained for the compound **17** with a concentration of 100 ppm with a rate of inhibition that reaches 99.57% (Table-2).

TABLE-2
EVOLUTION OF THE SPEED OF CORROSION AND THE RATE OF INHIBITION ACCORDING TO THE CONCENTRATION OF AZO-COMPOUNDS

C ppm	16		15		17	
	V_{corr} (mm/year)	R (%)	V_{corr} (mm/year)	R (%)	V_{corr} (mm/year)	R (%)
20	2.851	77.22	2.090	83.30	1.802	85.60
40	2.226	82.22	1.867	85.08	1.388	88.91
60	2.040	83.70	1.356	89.16	1.324	89.42
80	1.990	84.10	1.275	89.81	1.178	90.59
100	0.394	96.85	0.203	98.37	0.053	99.57
120	1.597	87.24	1.242	90.07	0.157	98.74

Influence of the concentration on the rate of phosphorus compounds inhibition

The best output for the family of phosphorus compounds in the same conditions is obtained for the compound **4** with a concentration of 80 ppm with a rate of inhibition that reaches 99.80% (Table-3).

TABLE-3
EVOLUTION OF THE SPEED OF CORROSION AND THE RATE OF INHIBITION ACCORDING TO THE CONCENTRATION OF PHOSPHORUS COMPOUNDS

C ppm	2		3		5		4	
	V_{corr} (mm/year)	R (%)	V_{corr} (mm/year)	R (%)	V_{corr} (mm/year)	5 (%)	V_{corr} (mm/year)	R (%)
20	5.298	57.68	1.971	84.25	0.434	96.53	0.214	98.29
40	4.987	60.16	1.572	87.44	0.372	97.02	0.200	98.40
60	2.286	81.74	1.469	88.26	0.186	98.51	0.131	98.95
80	1.896	84.85	0.875	93.01	0.052	99.58	0.024	99.80
100	1.225	90.21	0.696	94.44	0.075	99.40	0.046	99.63
120	1.152	90.79	0.475	96.20	0.324	97.41	0.200	98.40

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