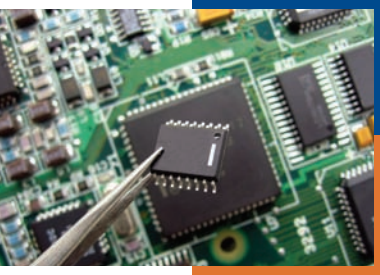
# *Phosphorus Chemistry*




- **Phosphines** to increase nylon performance while reducing processing costs
- **Phosphine** derivatives as anti-oxidants, flame retardants, and corrosion inhibitors
- **Chloro-phosphine** building blocks for organo-metallic catalysts

NOVOLYTE technologies

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**For contact information go to www.novolyte.com**

Novolyte Technologies is the former Fine Chemicals Division of Ferro Corp.

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OSR-140

Registered Firm
ISO 9001:2000


# Introduction

## If you would like to improve the performance and color of your nylon, while increasing process efficiency to reduce costs, we believe you are in the right place. And we believe that Novolyte Technologies is the right company to help.

If you are looking to construct more cost effective catalysts, phosphorus building blocks from Novolyte may help.

Novolyte Technologies is the former Fine Chemicals Division of Ferro Corp. Novolyte, located in Zachary, Louisiana, first offered benzene phosphinic acid as catalyst and polymer additive to the nylon industry in 1983 – under the Grant Chemical name. Since that first foray into the specialty phosphorus market, Novolyte has established itself as a reliable supplier of aryl phosphorus derivatives to industrial consumers. This area continues to grow, and Novolyte now provides both reactive intermediates and finished products to the polymer industry.

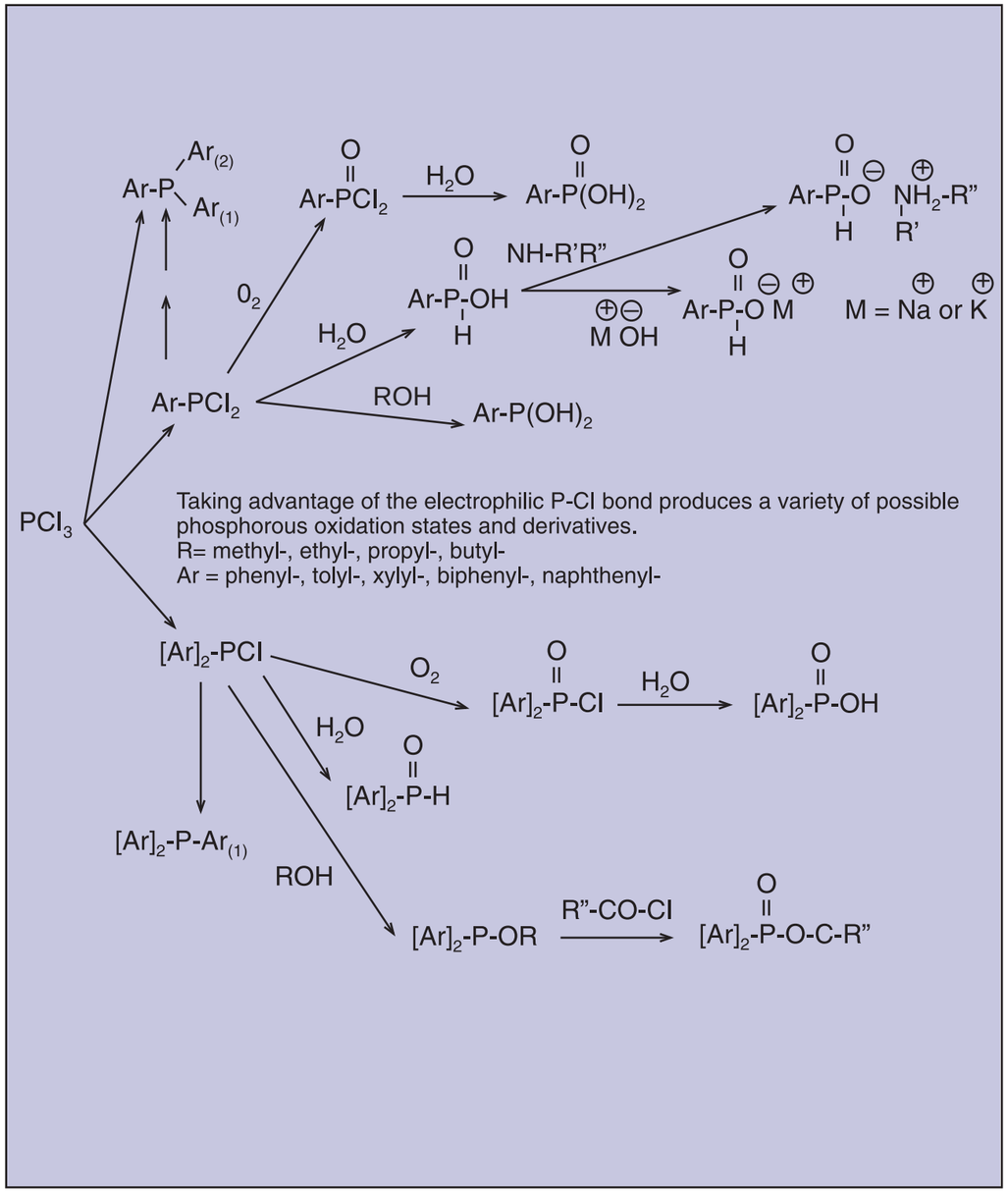
Novolyte Technologies relies heavily upon customer input for the development of new products. The current Novolyte has learned from forty years of experience as a provider of performance chemicals to meet the chemical needs of our customers and is working hard to build upon that tradition.

Please call to discuss your needs. Novolyte can perform batch reactions, distillation, extraction, crystallization, filtration, drying and mixing. The staff and facilities at Novolyte enable R & D programs to be cost-effective and responsive to our customer's needs. Novolyte's on-site pilot plant capabilities permit evaluation of technical feasibility and commercial potential of new products and processes before initiating production in commercial scale equipment. Equipment capabilities within process R & D include glass-lined, nickel-clad and stainless steel reactors jacketed for heating by high pressure steam or hot oil. Novolyte has been ISO 9002 certified for each of its nine operating units since 1992. Novolyte specializes in customer support and has experience with a variety of commercial and proprietary products that include metal stearates, glycol ethers, and cyclic ethers in addition to these phosphorus products. So, why not let Novolyte work with you to develop cost effective solutions for your applications and provide that competitive edge for your products and services? Let us know how we can assist you!

**www.novolyte.com**

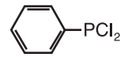
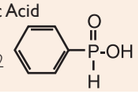
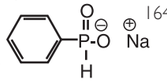
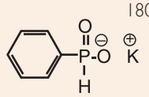
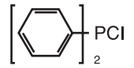
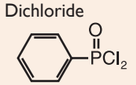
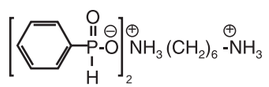
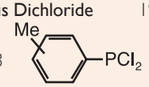
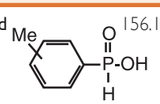
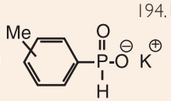
Please contact us to request more information about any of our products or to request samples for evaluation. Or to start the joint development of the performance chemical that you need to formulate or serve as a reactive intermediate.

# Synthetic Routes to Aryl Phosphorus Compounds






# Selected Physical Properties

| | Mol. Wt. | Min. Purity Wt% | Sp.Gr. @ °C | Crystallization Point | Boiling Point @ °C | Water Sol. @ 25°C; wt% | Appearance |
|---|---|---|---|---|---|---|---|
| **Benzene Phosphonous Dichloride** (BPD) CAS No.: 644-97-3  | 179 | 99.5 | 1.315 @ 25 | -51°C | 224°C @ 1 atm | Decomp. | clear, water white liquid |
| **Benzene Phosphinic Acid** (BZPA) CAS No.: 1779-48-2  | 142.1 | 97.0 | 1.38 @ 29 | 82-87 | Decomp. | 7.7 | white crystals |
| **Sodium Benzene Phosphinate** (Na-BZPA) CAS No.: 4297-95-4  | 164.1 | 97.0[a] | 1.22[b] @ 20 | >220 Decomp. | Decomp. | >50 | white crystals |
| **Potassium Benzene Phosphinate** (K-BZPA) CAS No.: 16263-37-9  | 180.1 | 97.0[a] | 1.22[b] @ 20 | >220 Decomp. | Decomp. | >50 | Sold in 50wt% aqueous solution |
| **Diphenyl Phosphonous Chloride** (DPC) CAS No.: 1079-66-9  | 220.6 | 96.0 | 1.229 @ 20 | ND[c] | 320 @ 1 atm | Decomp. | clear, light yellow liquid |
| **Benzene Phosphonic Dichloride** (BPDO) CAS No.: 824-72-6  | 195.0 | 99.0 | 1.375 @ 20 | 3 | 258 @ 1 atm | Decomp. | colorless liquid |
| **Hexamethylenediammonium bis Benzene Phosphinate** CAS No.: 5139-88-8  | 400.5 | 97.0[a] | ND[c] | ND[c] | >205 @ 1 atm Decomp. | >90.6 @ 30° | sold in 50 wt% aqueous solution |
| **Toluene Phosphonous Dichloride** (TPD) CAS No.: 28853-36-3  | 192.9 | 99.5 | 1.257 @ 20 | ND[c] | 242 @ 1 atm | Decomp. | clear, colorless liquid |
| **Toluene Phosphinic Acid** (TOPA) CAS No.: 4271-13-0  | 156.1 | 97.0[a] | ND[c] | 55-60 | Decomp. | 2.4 | white crystals |
| **Toluene Phosphinate** (M-TPA salts) CAS No.: 73276-99-0  | 194.1 | 97.0[a] | 1.22[b] @ 20 | ND[c] | Decomp. | >50 | sold in 50 wt% aqueous solution |

a) Purity based on corresponding phosphinic acid spec.;
b) Specific gravity of 50 wt% aqueous solution; c) Not Determined

# Commercial Product Packaging

| Product Name | Type of Packaging for Commercial Quantities |
|---|---|
| Benzene Phosphonous Dichloride (BPD) | Tank Trucks, 500 lb HDPE Drums |
| Toluene Phosphonous Dichloride (TPD) | 500 lb HDPE Drums, 5 gal HDPE Pails |
| Potassium Benzene Phosphinate 50 wt% Solution in Water | 3000 lb Tote Tanks, 500 lb HDPE Drums |
| Sodium Benzene Phosphinate 50 wt% Solution in Water | 3000 lb Tote Tanks, 500 lb HDPE Drums |
| Potassium Toluene Phosphinate 50 wt% Solution in Water | 500 lb HDPE Drums |
| Benzene Phosphinic Acid (BZPA) | 50 lb in PE bags inside Fiber Drums |
| Diphenyl Phosphonous Chloride (DPC) | 500 lb HDPE Drums |
| Hexamethylenediammonium bis(benzenephosphinate) (HMDA) | Tank Trucks, 3000 lb Tote Tanks, 500 lb HDPE Drums |

**Laboratory samples are available for all these products

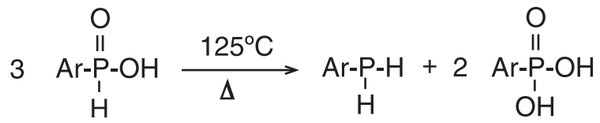
# Safety

## General Notes of Caution for Handling Organophosphorus Compounds

All organophosphorus compounds should be used in a manner that is in keeping with good chemical hygiene practices. Organophosphorus compounds should be handled only by trained personnel using adequate personal protective equipment and engineering controls, as well as exposure monitoring in keeping with applicable OSHA standards:

1. Avoid exposure to vapors, mists or dust.
2. Avoid all skin contact. Remove contaminated clothing and wash skin immediately with soap and water. Since in many instances organophosphorus compounds may be readily absorbed through the skin, particular attention should be given to the MSDS handling requirements for a particular compound.
3. Temperature excursions at or above the decomposition temperature for phosphinic acids and their derivatives require special precautions. The disproportionation reactions of these intermediate oxidation states of phosphorus often form pungent and colorless phosphines that are toxic.

For example, phenyl phosphine is a clear, colorless liquid with a foul odor that has been reported to resemble amines and acrylates. Concentrations of 0.57 ppm were readily detected by a human panel. Phenyl phosphine is miscible in organic solvents and insoluble in water. The LC50 (Lethal Concentration that kills 50%) for rats was 38 ppm. Signs of exposure could include excessive salivation, uncontrolled and excessive tear formation and/or labored respiration. A EL (i.e. Permissible Exposure Limit) of 0.05 ppm is recommended by OSHA.






# Summary of Organophosphorus Applications

## a. Phosphine Derivatives:

Major commercial applications for these compounds depend upon the ability of phosphines to modulate transition metal catalyzed reactions and to function as antioxidant additives. The superior Lewis basicity of the lone pair of electrons on phosphines increases both their reducing capacity as well as their ability to form strong coordination bonds to various transition metals. For antioxidant applications, this Lewis basicity, coupled with strong P-O bonds results in the facile reaction of phosphines with oxygen and oxygen containing radicals (i.e. O and OOR). Superior electron donating ability and polarizability make phosphines strong ligands for stabilizing transition metal geometries and oxidation states. Phosphine ligands are often used to enhance catalyst selectivity (i.e. asymmetric synthesis) as well as improve turnover numbers for expensive transition metal catalysts.

Quaternization of phosphines provides phosphonium ions that find application as phase transfer catalysts, detergents, flame retardants and biocides. Since phosphorus is a third row element it is both larger and more polarizable than nitrogen. These properties help to make phosphonium salts more soluble in organic media which improves the lipophilic character of phosphonium salts relative to their ammonium analogs, an important consideration in biocide applications

Phosphonium compounds are used to impart ignition resistance to cellulosics as well as polyesters, polyamides and polyethers. Flame retardancy applications of these and other phosphorus compounds affect the rate of combustion by at least two mechanisms. Phosphorus derivatives can retard the rate of fuel production along the combustion front, or they may increase the charring of polymer that produces a physical barrier resistant to both heat transfer and permeability of gaseous decomposition products necessary to fuel the combustion process.

Phosphine oxides find commercial application in the areas of metal recovery and as flame retardant additives. In addition, phosphine oxides also are useful complexing agents in the recovery of organic compounds such as carboxylic acids, alcohols and phenols from effluent streams.

## b. Phosphinic Acid Derivatives:

Commercial uses of phosphinic acid derivatives have focused on the complexing and antioxidant properties of these compounds. The complexing ability of these derivatives is useful for metal recoveries from acidic waste streams. Phosphinic acids are also useful as dispersants and find application in dispersing microencapsulated inks for pressure sensitive copying paper. Phosphinic acids are also useful as curing accelerators for peroxide initiated cross-linking and as initiators in the peroxide initiated emulsion polymerization of diene and acrylate derivatives

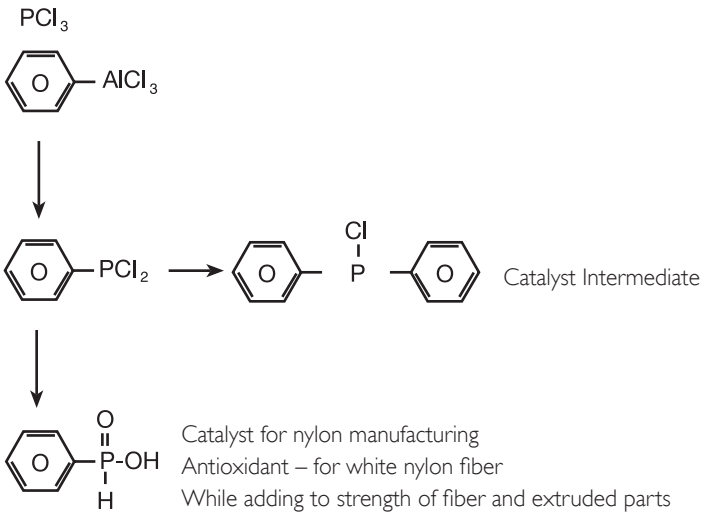
Phosphinic acid derivatives are useful in protecting metal surfaces against corrosion. For example, phosphinic acid additives provide improved polyphenylthioethers lubricity for steel-steel and chromium-anodized aluminum contacts along with improved thermal stability for these lubricants. Derivatives of phosphinic acid are also used to improve the performance of high temperature greases. This strong interaction of phosphinic acids with metal surfaces also finds application in mold release formulations.

Grafting phosphinic acids onto various polymers such as unsaturated polyolefins, polyesters and cellulosic fibers makes such polymers flame resistant. As a result of grafting, fire retardant properties become an integral part of the material and not susceptible to migration or phase separation within a polymer matrix as additives tend to perform.

Phosphinic acids have also been used to stabilize polymer melts of polyamides. Even for thermoplastics such as polypropylene, addition of phosphinic acids helps reduce coloration that occurs both from manufacture and processing of these polymers. In these applications it is probably a combination of phosphinic acid's ability to complex with catalyst residues as well as the antioxidant properties of phosphinic acids themselves that help to retard degradation of polymers. The antioxidant properties of phosphinic acid additives have been used to extend the shelf life of photo-crosslinkable polyester and urethane resins.

In low concentrations (i.e. 10- 6 to 10- 7 M) phosphinic acids have been found to be phytoactive in stimulating root growth. In higher concentrations, these acids become soil disinfectants and are useful in controlling bacterial infestations that adversely effect plant growth and development.

## What can Novolyte Phosphorus Do for You?




Catalyst for nylon manufacturing
Antioxidant – for white nylon fiber
While adding to strength of fiber and extruded parts

NOVOLYTE technologies

Manufacturing
111 West Irene Road
Zachary, LA 70791
(225) 654-6801
Fax: (225) 654-3268
www.novolyte.com

customerservice@novolyte.com
8001 East Pleasant Valley Rd.
Independence, OH 44131
(216) 867-1050