

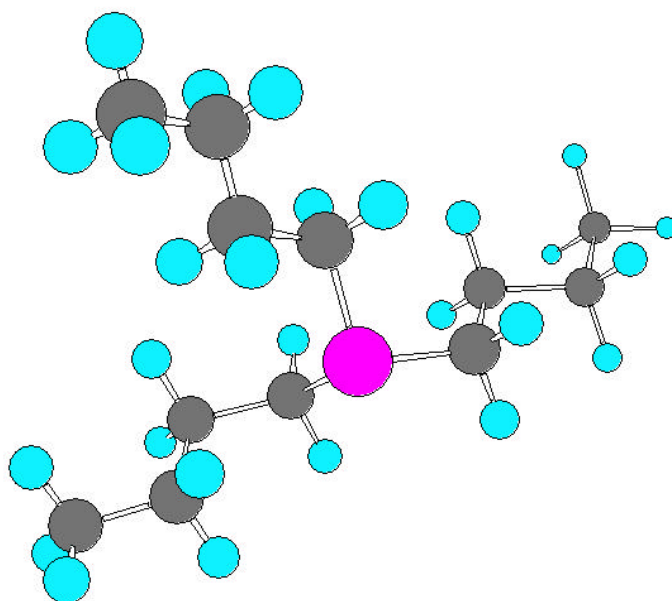
# CYTEC

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## CYTOP® 340

### Organo-Phosphine

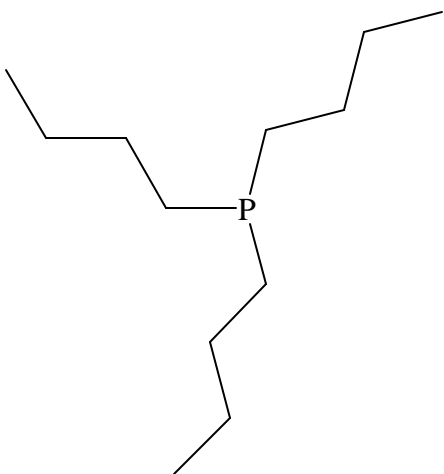


**Trade Name:** ..... **CYTOP® 340**

**Chemical Name:** ..... tri n-butylphosphine

**C.A.S. Number:** ..... [998-40-3]

**Registration:** ..... EINECS ( 213-651-2 ), TSCA, DSL, ENCS, AICS, PICCS



**CYTOP 340** is a colorless mobile liquid and unlike some of the lower homologues, because of the very low vapor pressure, it has only a slight odor. It is a strong reducing agent and although classified as pyrophoric, it is borderline pyrophoric.

Tributylphosphine is very nucleophilic and can be readily protonated to convert it into air-stable salts. The latter are very convenient to deal with on a bench scale and provide an alternative source of tributylphosphine for many reactions (23).

Cytec currently produces **CYTOP 340** on a multi-ton scale and it is commercially available in 317 kg /700 lb units packaged in returnable 100 imperial gallon steel cylinders. Smaller 5 to 30 kg quantities in returnable SS cylinders for pilot scale studies are also available on request. Both the commercial size and pilot size cylinders are fitted with dip-tubes and head space ports to allow facile transfer of the product under an inert gas. Small scale samples ( 200 ml to 2000 ml units ) in non-returnable steel bottles are available for evaluation purposes.

### **Physical Properties:**

Boiling point .....	240 °C ( 760 mm Hg )
	130 °C ( 20 mm Hg )
Melting point .....	-60 °C
Flash point ( closed cup ) .....	93 °C
Auto ignition temperature .....	168 °C
Specific gravity .....	0.81 @ 20 °C

## Toxicological Data:

Acute oral LD50 ( rat ) ..... 750 mg/kg  
Dermal LD50 (rabbit ) ..... >2000 mg/kg  
( Mild transient ocular irritant )

## Transportation Data:

WHIMIS ..... Class B Div. 6 – Reactive Flammable Material  
Class D Div. 2B Toxic  
Shipping Class ..... 4.2  
UN Number ..... 3254

A complete MSDS for **CYTOP 340** is available on the following Cytec web site [http://www.cytec.com/msds/BB/Bb\\_msds.htm](http://www.cytec.com/msds/BB/Bb_msds.htm). Additional handling information is documented in “Storage and Handling Recommendations of Alkylphosphines”. Copies are available on request; refer to document # SPT-151-A.

## Sales Specifications:

There are two grades of **CYTOP 340** – “Regular” and “High Grade”. The sales specifications for each are set out in Table 1.

**Table 1**

### **CYTOP 340 Sales Specifications**

	<b>Regular Grade</b>	<b>High Grade</b>
Tri butylphosphine	>93.5%	>94.5%
Total tributylphosphine isomers	>97%	>98%
Di butylphosphine isomers	<0.2%	<0.15%
Mono butylphosphine isomers	0.0%	0.0%
Tributylphosphine oxide	<1%	<0.4%
Nitriles	not reported	<0.2%
Colour (A.P.H.A.)	<100	<50

## Composition:

**CYTOP 340** is prepared via the free radical addition of phosphine to butene-1. While this route affords mainly tri butylphosphine - typically 94%, the nature of the radical route also yields some unique byproducts.

In the presence of free radical initiators, the addition of phosphine to alpha olefins is normally in the anti-Markownikoff sense – that is phosphorus adds to the terminal carbon ( 30, 31 ). However, there is a small fraction of the addition which proceeds in the “normal” Markownikoff mode – that is phosphorus adds to the beta carbon. In the case of phosphine addition to butane-1, this typically results in the formation of 2.5 to 3.5% dibutyl(mono sec-butyl)phosphine.

Additionally, while chain transfer predominates over polymerization during the free radical addition of phosphine to olefins, there is a very small fraction of beta carbon radical addition to butane rather than proton abstraction. This typically results in the formation of 0.5 to 0.7% of dibutyl(2-ethylhexyl)phosphine.

Reaction conditions are such that monobutylphosphine isomers are essentially zero (<0.01%) and dibutylphosphine isomers are typically <0.2%.

While tributylphosphine oxide is reported on the certificate of analysis, the actual existence of reported levels is questionable. Because of the reducing nature of tributylphosphine, extreme precautions are required when sampling and analyzing **CYTOP 340** for oxide content. This is evident from a rather large standard deviation for the oxide analysis vs. that for the other components. The actual oxide content is likely considerably less than reported values.

The minor nitrile-containing components observed in **CYTOP 340** are the result of free radical initiator decomposition products coupling with each other or from the addition of such radical moieties to butene.

## Analytical Procedures:

Gas chromatography is the recommended technique for **CYTOP 340** analysis. All components are volatile and are thermally stable. They readily elute from low polarity columns. TCD and FID are both suitable means of detection and quantification. Mass selective detectors ( MSD ) are ideal for component identification.

Figure 3 contains a typical G.C. trace for **CYTOP 340**. The components are identified in Table 1. The column is a 30 meter X 0.53 mm DB-5. The initial oven temperature is 50 °C for one minute followed by a heating rate of 10 °C to 290 °C. The injector and detector ( FID ) are at 300 °C. The carrier gas is helium and is maintained a constant head pressure of 9 psig. The injection size is 0.1 µ litre and is essentially splitless.

Phosphorus NMR, while suitable for approximate quantification and identification, is much less precise than gas chromatography. Additionally, if samples are diluted with solvents, care must be taken to initially purge the solvent free of oxygen. This is especially so for very dilute solutions.

Figure 4 contains a typical **CYTOP 340** <sup>31</sup>P NMR spectrum. The components are identified by their respective chemical shifts in Table 2.

## Oxidation:

**CYTOP 340** must be handled under inert conditions at all times to avoid oxidation. Dinitrogen or argon are recommended for inerting vessels. The standard shipping containers which are fitted with a discharge dip tube and head space port are ideal for transferring **CYTOP 340** using inert gas pressure. With the proper piping design, there will be no exposure to air. However, small laboratory samples, which are generally packed in steel cylinders fitted only with a head space port, will require more precautions when extracting samples.

One typically would expect to observe tributylphosphine oxide as the main reaction product on exposure of **CYTOP 340** to air. This is certainly the case when tributylphosphine is treated with dilute hydrogen peroxide. Quantitative yields of tributylphosphine oxide are obtained.

However, on oxidation of trialkylphosphines with air, a variety of oxygen containing compounds are observed ( 32 ). Tributylphosphine oxide is generally the major component – typically 50 to 55%. However, dialkylphosphinate esters are also formed - typically 40% with lesser amounts of phosphonate esters and phosphate esters. Other non-phosphorus containing products are olefins and alcohols. Oxidation of trialkylphosphines with air is not a clean reaction.

## Applications:

**CYTOP 340** is an extremely versatile reagent which goes into a variety of applications such as simple desulfurizations and disulfide reductions or as a catalyst ligand for Heck and Suzuki coupling reactions, and more recently as a processing aid to replace triphenylphosphine in the Staudinger and Mitsunobu reactions.

As an intermediate, **CYTOP 340** is readily quarternized to a variety of phosphonium salts which find utility as phase transfer catalysts ( PTCs ), biocides or for the synthesis of specific Wittig reagents. While tributylphosphine oxide has little practical utility, the corresponding sulfide prepared from **CYTOP 340** and elemental sulfur is a liquid at room temperature and is an excellent solvent extractant for various “soft” metals like gold, silver, mercury, cadmium and palladium.

**Desulphurization:** Because **CYTOP 340** is a powerful reducing agent, it can readily remove sulfur from a variety of organic compounds ranging from API intermediates (1) to low grade fuels (2,3). Capps et al describe the enthalpies for the transfer of sulfur, selenium and tellurium from organic substrates to various tertiary alkylphosphines – including tributylphosphine (4).

**Disulfide reduction:** Disulfide bonds are readily reduced under mild conditions using trialkylphosphines such as **CYTOP 340**. A practical application of this is in the manufacture of Omapatrilat (5,6).

**Mitsunobu Condensations:** The Mitsunobu reaction is a facile route to condensation products like esters or amides which occurs under very mild conditions. Key to this synthesis is the removal of water via an oxygen acceptor ( tertiary phosphine ) and a hydrogen acceptor ( diazo compound such as diisopropylazodicarboxylate – DIAD ).

Earlier publications describing the application of the Mitsunobu reaction involved the use of triphenylphosphine (TPP) as the oxygen acceptor. As a consequence of the condensation reaction, the byproducts are triphenylphosphine oxide (TPPO) and a hydrazine. Both of the above require separation from the condensation product. The hydrazine is typically removed using an acidic aqueous scrub. TPPO, on the other hand is a very insoluble solid which requires a solid/liquid separation. More often than not, the product is also an insoluble solid which complicates the separation.

Substitution of tributylphosphine ( [CYTOP 340](#) ) for TPP has several advantages:

- 1) It is a liquid and consequently is much easier to transfer on a large production scale than a solid like TPP.
- 2) The resulting tributylphosphine oxide (TBPO) is somewhat water soluble and, in general can be removed by a water wash. Because TPPO is essentially a very insoluble solid, contamination of solid APIs or API intermediates can be a serious issue. Partitioning of tributylphosphine oxide between organic and aqueous layers is discussed in more detail in the section entitled “Extraction of Tributylphosphine Oxide”
- 3) Tributylphosphine is a much more powerful oxygen acceptor and less hindered than TPP. Consequently in many instances tributylphosphine demonstrates considerably faster kinetics and better yields (15).

One possible negative comment is that tributylphosphine is “pyrophoric” and is more difficult to deal with than the more air-stable TPP. While this statement may hold true for bench scale synthesis, it becomes a non-issue when working on a manufacturing scale. [CYTOP 340](#) is shipped in metal cylinders fitted with a dip-tube and a head space port. The material is readily transferred under an inert gas ( dinitrogen or argon ) to an inerted reactor. On the other hand, the solid TPP must be dissolved in a suitable solvent prior to charging to the reactor.

Following are some recent references relating to the use of tributylphosphine as an oxygen acceptor in Mitsunobu reactions (7-20, 33-34,51,54 and 55). Mechanistic studies on the use of tributylphosphine are reported in references 18,19 and 20.

**Catalyst Ligand for Heck and Suzuki Coupling:** Bulky ligands are generally preferred for Suzuki coupling reactions. However, tributylphosphine in combination with bulky N-heterocyclic carbenes also gives excellent results (21). G. Fu et al have reported excellent Suzuki cross-coupling yields from boronic acids with aryl and vinylchlorides and aryltriflates (22). Harayama et al have recently reported the use of Pd(OAc)<sub>2</sub>/P(Bu)<sub>3</sub> catalyst systems for the coupling of aryltriflates and iodides with arenes (24-26).

As reported by G. Fu et al, Pd/P(Bu)<sub>3</sub> catalyst are also effective for Heck reactions (27).

Another related application using Pd/P(Bu)<sub>3</sub> catalysts systems is the preparation of tri-aryl amines via the cross-coupling of diarylamines and arylhalides (28).

**Amination Catalyst Ligand:** Recently R V Chaudhari et al have reported the use of a CuI/tributylphosphine catalyst system for the synthesis of tertiaryarylamines by the amination of arylhalides. Yields and kinetics are considerably than previously reported studies in which TPP was used as a ligand. (56).

**Catalyst ligand for the Diels-Alder 1,4 hydrosilylation reaction:** Gerhard Hilt et al have high yields for cobalt(1) catalysed Diels-Alder 1,4-hydrosilylation of 1,3 dienes. High regioselectivity was achieved when using tributylphosphine as the catalyst ligand (59).

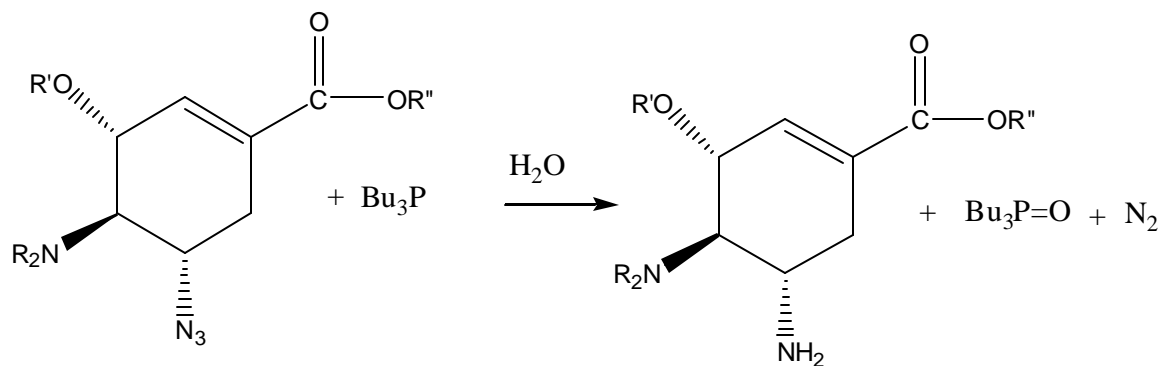
**Wittig Reactions:** The Wittig reaction is an excellent route to isomeric internal olefins from alkylhalides and aldehydes via phosphorous ylids. The intermediate ylid is formed by base abstraction of an acidic alpha proton from a phosphonium salt which in turn results from the nucleophilic addition of a tertiaryphosphine ( generally TPP ) to an alkyl halide. The ylid and aldehydes then react to yield the desired internal olefin and TPPO as a byproduct (58).

TPP has historically been used as the tertiaryphosphine because it contains no alpha protons and the resulting ylid can only yield the product containing the alkyl moiety from the original alkylhalide. In general, any ylid resulting from the combination of tributylphosphine and an alkylhalide can yield a mixture of two products – one containing the desired alkyl group from the alkylhalide or a “butyl” moiety since there is a distinct probability of abstracting an acidic proton from any of the four substituents attached to phosphorus. Thus tributylphosphine is not useful as a “generic” precursor for Wittig reactions.

However, there are many cases in which [CYTOP 340](#) can be used ( and indeed is more desirable ). An obvious case – but very rare – is when one desires a “butyl” moiety on the olefin. There are also many instances in which it is desirable to have a methyl or ethyl ester beta to the olefinic site. In this case, the phosphonium salt will have the generic structure  $[R_3P-CH_2-C(O)OR]^+ X^-$  and the proton alpha to the ester will be much more acidic than any alpha proton on R. Thus if R=butyl, the resulting ylid will always be  $Bu_3P=CHC(O)R'$  and never  $Bu_2(R'(O)CCH_2-)P=CHCH_2CH_2CH_3$  which in turn will yield  $R''CH=CH-C(O)R'$  in which R'' is derived from the aldehydes (35,36).

In addition to having a somewhat water soluble tertiaryphosphine oxide byproduct, the use of [CYTOP 340](#) in Wittig reactions generally yields faster kinetics, higher yields and improved E/Z ratios.

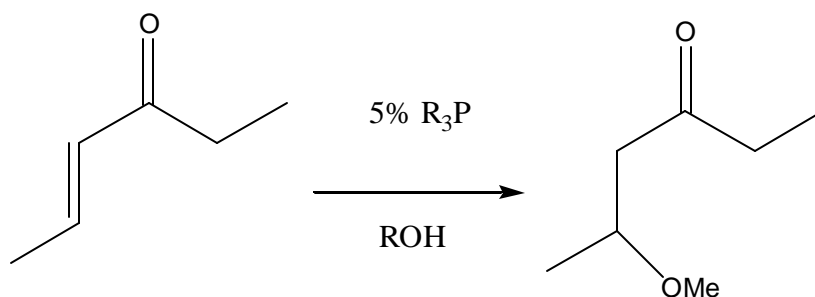
**Staudinger Reaction:** The Staudinger reaction is often employed to synthesize amines from azides. The reaction is facilitated by the use of a tertiaryphosphine ( usually TPP ) to form an intermediate phosphine imide which subsequently undergoes hydrolysis to yield the desired amine and TPPO as a byproduct. As in the case of the Mitsunobu reaction, the insoluble TPPO can cause difficulties in down stream work-up to recover the final product. Tributylphosphine has also been demonstrated to be an alternate to TPP in the Staudinger reaction ( 29,47), Scheme 1.



**Scheme 1: Staudinger reaction using [CYTOP 340](#) as the reducing agent**

The above applications represent stoichiometric applications for [CYTOP 340](#). The following applications are examples in which [CYTOP 340](#) partakes in organic synthesis but in a catalytic mode.

**Catalyst for the hydration and hydroalkoxylation of enones:** Recently Toste et al ( 37 ) have reported a general procedure for the hydration or hydroalkoxylation of enones according to Scheme 2.

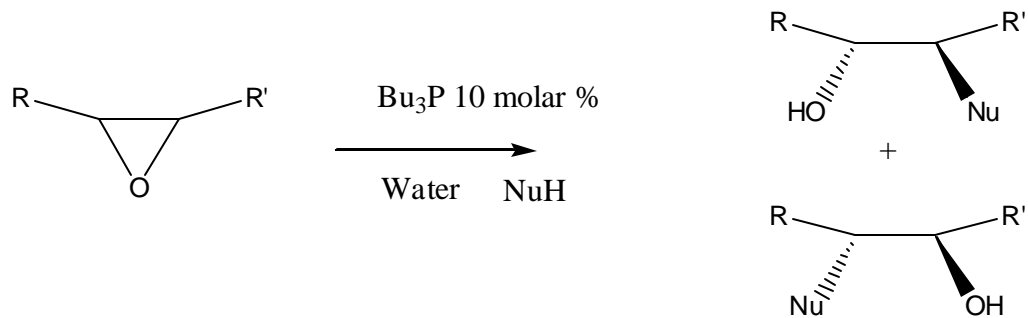


**Scheme 2: Hydroalkoxylation of Enones – D. Toste et al**

ROH can be water ( R = H), primary alcohol, secondary alcohol or a phenol. A proposed mechanism and limitations of the synthesis are documented.

**Bu<sub>3</sub>P catalyzed addition of nucleophiles to epoxides:** Xue-Long Hou and Ren-Hua Fan have reported novel nucleophile additions to epoxides and aziridines which are promoted by catalytic amounts of tri butylphosphine in an aqueous medium ( 38,57 ).

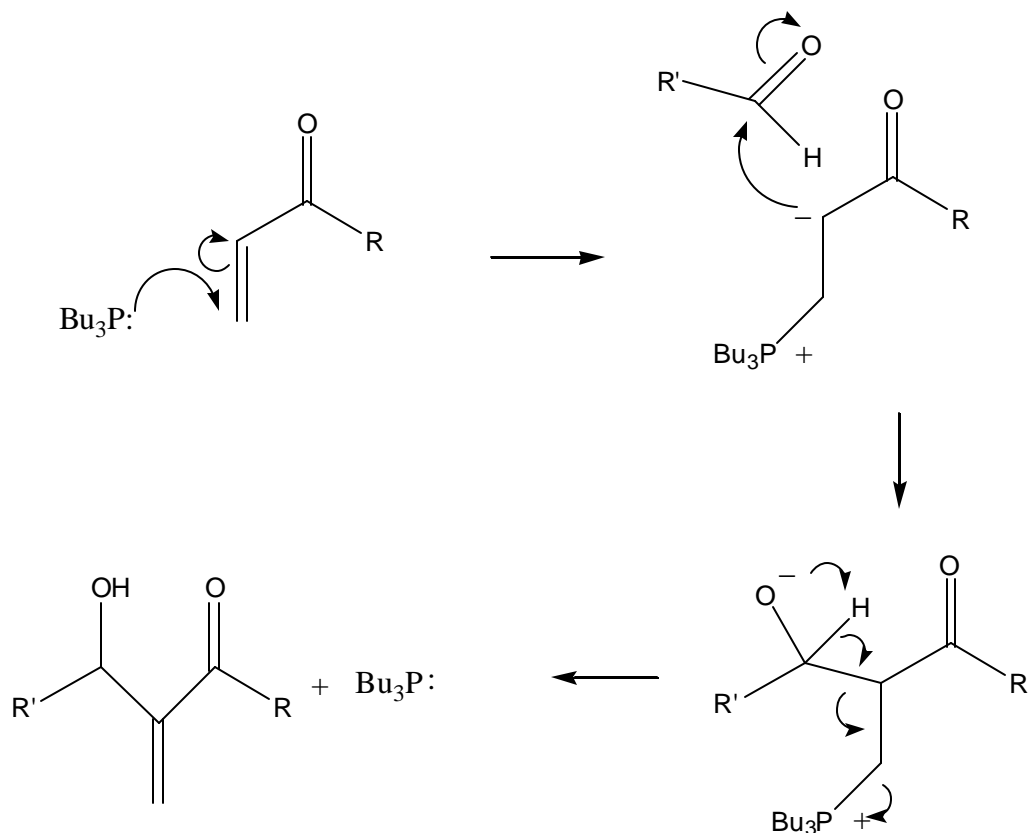
Normally, tertiary phosphines will deoxygenate with epoxides to form tertiaryphosphine oxides and an olefin ( 39 ). However, in the presence of nucleophiles and in an aqueous medium, the reaction pathway is completely altered according to Scheme 3.



**Scheme 3:  $\text{Bu}_3\text{P}$  promoted nucleophile addition to epoxides in an aqueous medium.**

In addition to promoting the reaction, the presence of tributylphosphine also controls the regioselectivity. An analogous reaction was also noted for aziridines. The authors also observed that the less hindered tributylphosphine was much more effective than tri cyclohexylphosphine and the less basic triphenylphosphine.

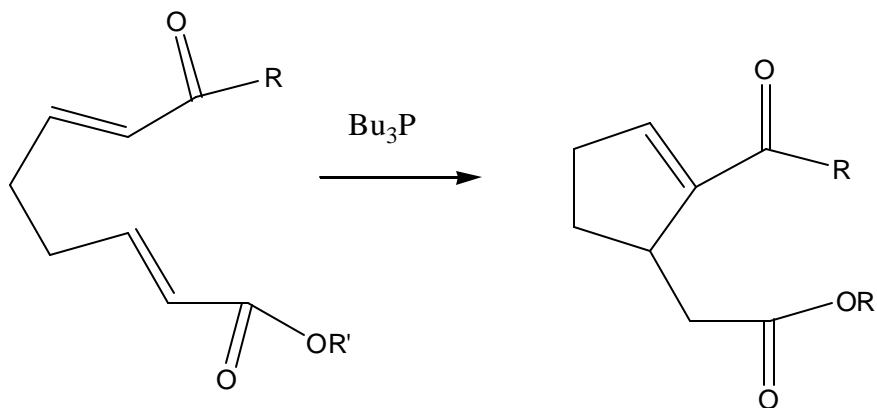
**Baylis-Hillman Reaction –  $\text{Bu}_3\text{P}$  catalyzed:** The well known Baylis-Hillmann reaction ( 48 ) in which aldehydes add to activated eneones is catalyzed by nucleophiles such as tributylphosphine ( Scheme 4 ). Recent chemical literature contains many practical synthetic applications using the Balyis\_Hillman reaction ( 49,50 ).



**Scheme 4 – Baylis-Hillman Reaction catalyzed by  $\text{Bu}_3\text{P}$**

As well as the standard Baylis-Hillman reaction, there are many variations on this theme as outlined below.

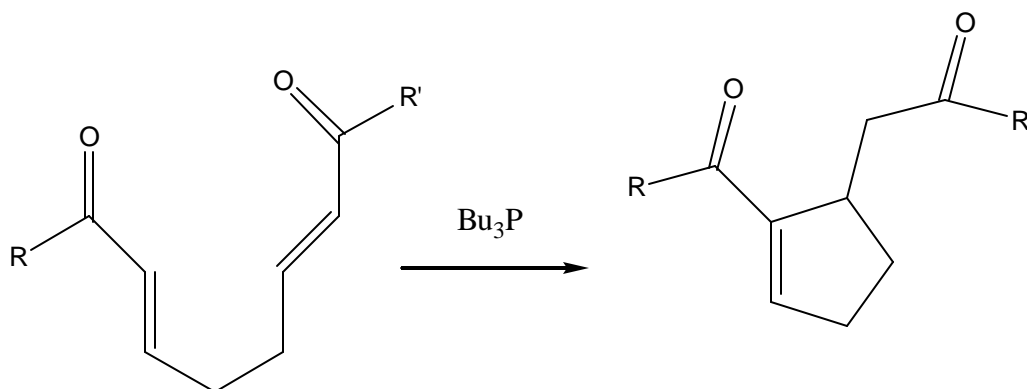
**Intramolecular  $\text{Bu}_3\text{P}$  promoter Morita-Baylis-Hillman Reaction:** Roush et al have reported a variation of the  $\text{Bu}_3\text{P}$  promoted Morita-Baylis-Hillman reaction in which catalytic amounts of low sterically hindered tertiary phosphines generate cyclopentenones from intramolecular reactions of enone/enoate substrates according to Scheme 5 (40).



### Scheme 5: $\text{Bu}_3\text{P}$ promoted intramolecular Morita-Baylis-Hillman reaction

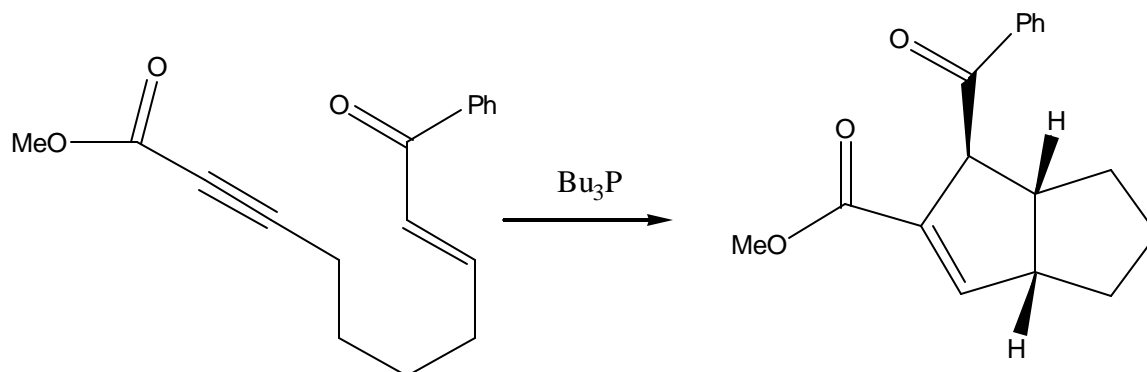
This reaction works best with  $\text{Me}_3\text{P}$  but almost equally well with the much less hazardous and readily available  $\text{Bu}_3\text{P}$ .

**$\text{Bu}_3\text{P}$  promoted cyclopentene formation from an intramolecular Rauhut-Currier reaction:** Krische et al have reported an analogous synthesis of cyclopentenes by the  $\text{Bu}_3\text{P}$  promoted intramolecular Rauhut-Currier reaction using bis enones ( 41,42 ). See Scheme 6.



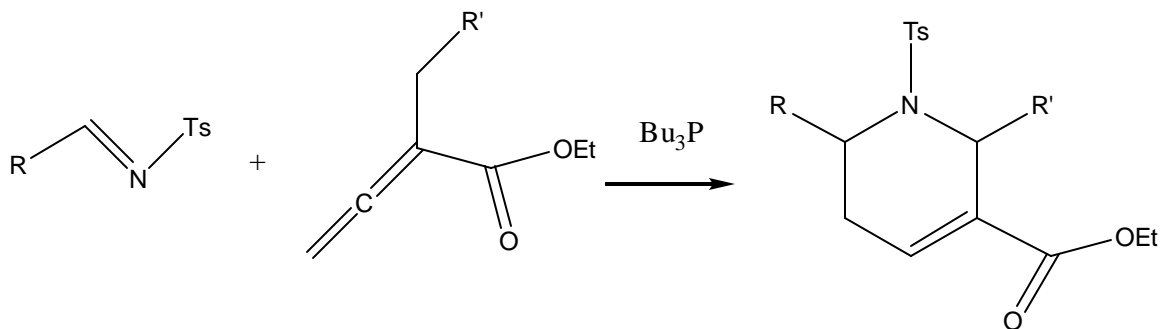
### Scheme 6: Cyclopentenes from bis enones via an intramolecular Rauhut-Currier reaction.

**$\text{Bu}_3\text{P}$  promoted [3+2] cycloadditions of mono-enone/mono-yne systems:** Krische et al have also demonstrated the diastereoselective synthesis of diquinanes from the  $\text{Bu}_3\text{P}$  promoted intramolecular cyclization of enone/ynoates ( 43 ) according to Scheme 7.



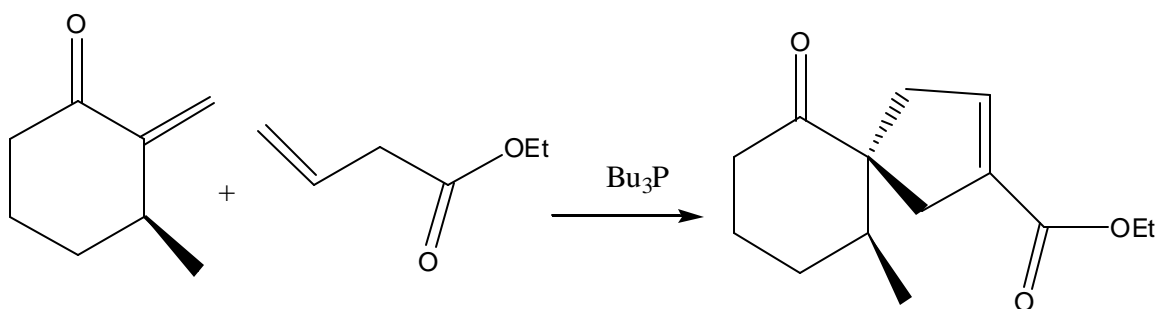
### Scheme 7: diquinanes from the $\text{Bu}_3\text{P}$ promoted intramolecular cycloaddition of enone/ynones

**Tetrahydropyridines from  $\text{Bu}_3\text{P}$  promoted [4+2] annulation of butadieneoates and N-tosylbenzylidimines:** Another example of  $\text{Bu}_3\text{P}$  promoted reactions of activated olefins is the [4+2] annulation of butadieneoates and N-tolylbenzylidimines to form unsaturated pyridines. Kwon et al. recently disclosed the above reaction as presented in Scheme 8. ( 44 )



**Scheme 8: Tetrahydropyridines from the  $\text{Bu}_3\text{P}$  promoted [4+2] annulation of butadieneoates and N-tolylbenzylidimines**

**Total Synthesis of (-)-Hinesol: an example of a  $\text{Bu}_3\text{P}$  promoted [3+2] cycloaddition reaction of 2,3-butadieneoate to electron deficient alkene:** A further example of the usefulness of  $\text{Bu}_3\text{P}$  as a catalyst is the formation of cis-spirovetivanes from cyclic enones and electron deficient olefins as reported by Yishu Du and Xlyan Lu ( 45 ). See Scheme 9.



**Scheme 9: Synthesis of cis-spirovetivanes by  $\text{Bu}_3\text{P}$  promoted [3+2] cycloadditions of cyclic enones and 2,3-butadieneoates.**

**CYTOP 340 as a General Reagent in Organic Synthesis**

In addition to the above reactions, numerous other examples of the general use of CYTOP 340 as a general reagent for organic synthesis are cited in two recent reviews by Valentine et al ( 52,53 )

**Removal of palladium catalyst from reaction products:** One of the key issues concerning synthetic chemists using metal catalysts in such reactions as the Suzuki coupling reaction is the eventual separation of the palladium from the reaction product. There is no universal efficient means to accomplish this. However, a recent paper by Paul O'Shea et al ( 46 ), demonstrates the utility of using **CYTOP 340** to form an organic soluble complex which can be extracted from aqueous solutions containing the Suzuki coupling product. This technique will not be generally applicable, but may be useful whenever the product is water soluble.

An alternate complexing agent which could be used in cases in which reaction products are water soluble is **CYTOP 380** – trioctylphosphine. Due to the higher carbon content, the latter is much more apt to partition into the organic layer. Organic soluble extractant reagents such as **CYANEX 471X** ( triisobutylphosphinesulfide ) may apply in such cases.

At the other extreme – cases in which the reaction products are organic soluble, water soluble tertiary phosphines such as tris (3-hydroxypropyl)phosphine may potentially be used to form a water soluble palladium complex which can be extracted with water from the organic soluble reaction product.

## Extraction of Tributylphosphine Oxide

Many applications of **CYTOP 340** result in the stoichiometric production of byproduct tributylphosphine oxide – e.g. Mitsunobu reactions and disulfide reductions as described previously. Consequently it is desirable to remove the oxide from the reaction medium.

In applications in which triphenylphosphine is used, the corresponding triphenylphosphine oxide is generally insoluble and is removed by filtration. Solid/liquid separations are generally labor intensive and if the desired reaction product is also insoluble, then one or more recrystallization steps will be required to further purify the desired product.

Tributylphosphine is soluble to some extent in most common organic solvents such as toluene and octane. However, it is more soluble in water. Because of this relative difference in partition coefficients, there is an opportunity to remove the tributylphosphine oxide from an organic liquid reaction mixture by aqueous extraction. The degree to which this technique will be practical will be very process dependant.

The following data is provided to give some guidelines for the removal of tributylphosphine oxide from general organic reaction mixtures. Two reaction solvent systems were chosen – octane and toluene. The extraction is carried out using de-ionized water or 90/10 solutions of either water/methanol or water/isopropanol. The effect of the pH of the aqueous phase is also discussed.

Figure 5 demonstrates the effect of the aqueous equilibrium pH on the % extraction of tributylphosphine oxide from toluene using various aqueous/organic ( A/O )

ratios. The aqueous pH was either adjusted to 0.1 with sulfuric acid, to 13.5 with NaOH or was left unaltered at the more neutral ambient pH. No alcohol was added to these systems. These were single contacts with A/O ratios of 1, 5 and 10. After vigorous shaking for 10 minutes at 10 °C, the phases were allowed to separate and the organic layers were analyzed for residual tributylphosphine oxide. The initial organic layer contained 100 g/l tributylphosphine oxide. The data indicated that, in general, less is extracted at high pH values but there is little difference between “neutral” to acidic pH values. Also if the organic layer is relatively polar such as toluene, then extractions with A/O ratios >5 should be used to be effective.

Figures 6 and 7 contain extraction isotherms from 67 g/l toluene and octane solvents. The aqueous layer was either de-ionized water, a 90/10 water/methanol mixture or a 90/10 water/isopropanol mixture. As above, the phases were contacted by vigorous shaking for 10 minutes at 20 °C using A/O ratios of 1,5,10 and 50. The relative concentrations in the aqueous layer are plotted vs. those in the corresponding organic phase along with proposed operating lines. The latter is simply an A/O ratio which may be used. An A/O ratio of 15 was chosen for the extraction from toluene ( Figure 6 ) while two operating lines at A/O ratios of 1.0 and 3.0 are plotted in Figure 7.

Based on the data in Figures 6 and 7, two things are immediately obvious: 1) extractions are much more efficient from non-polar organic solutions such as octane and 2) “pure” water is more effective than aqueous water/methanol or water/isopropanol solutions.

In the case of the toluene solution, three extractions with pure water and an A/O ratio of 15 will be required to reduce the tributylphosphine oxide from 100 g/l to less than 5 g/l in the organic phase. If a 90/10 water/methanol solution is used, then approximately four extractions will be required to obtain the same degree of extraction. However, an A/O ratio of at least 25 and many contact stages are required to similarly extract the phosphine oxide with a 90/10 water/isopropanol solution.

Extraction from non-polar organic solvents such as octane appears to be much less difficult. As above, “pure” water is preferred over water/methanol or water/isopropanol solutions. Even with an operating line of 1 ( 1/1 aqueous/organic extractions ), after three extractions, the tributylphosphine oxide will be reduced from 67 g/l to less than 2 g/l. As above, approximately four similar 1:1 extractions using 90/10 water/methanol will be required to accomplish the same effect. Also as above, water/isopropanol extraction solutions do not appear to be practical – at least four extractions using 3/1 aqueous/organic extractions will be required. Consequently the aqueous waste stream will be relatively large.

In summary, the liquid/liquid extraction of the byproduct tributylphosphine oxide appears to be practical from relatively non-polar organic matrices using pure water as the extraction medium. A 90/10 water methanol solution may be practical but water/isopropanol solutions do not appear practical. The pH should be slightly acidic. Depending on the degree of extraction required, 2 to 4 1/1 aqueous/organic extractions will be required.

## **Tributylphosphine oxide – ecotoxicity model data**

Modeling data predicted that the octanol/water partition coefficient ( Log  $K_{ow}$  ) for tributylphosphine oxide will be approximately 3.87. The indication being that there is potential for bio-accumulation.

The 96 hr LC50 for fish is estimated at 6.9 mg/L while the 48 hr EC50 and 86 EC50 values for daphnia and green algae are estimated at 3.4 and 2.4 mg/L respectively. Based on these estimates, it is expected that tributylphosphine oxide will be toxic to marine organisms.

Modeling experiments indicate that tributylphosphine oxide will biodegrade 70% over a 28 day period and therefore is not expected to persist in the environment.

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Figure 1:

**CYTOP 340 Vapor Pressure**

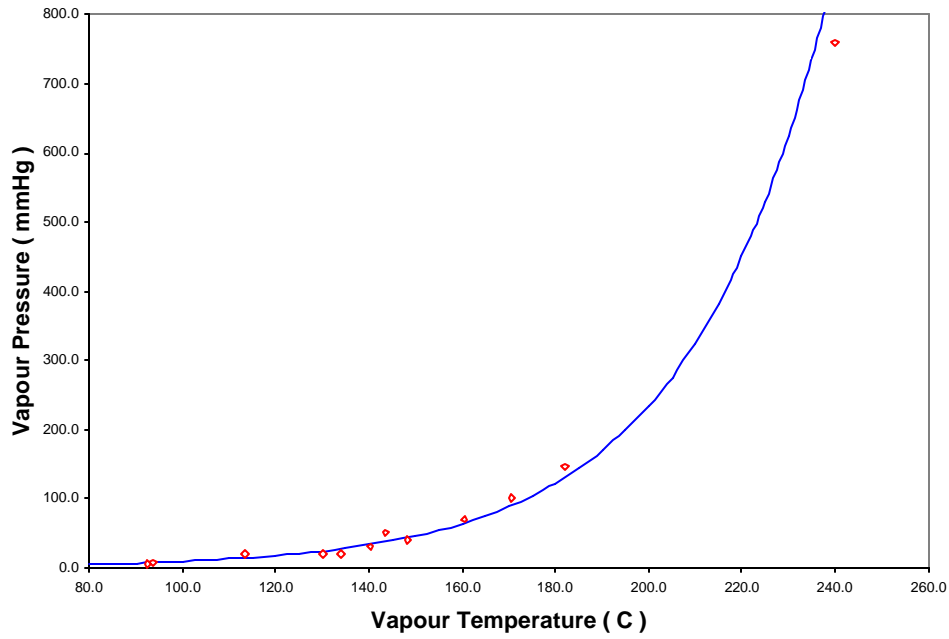
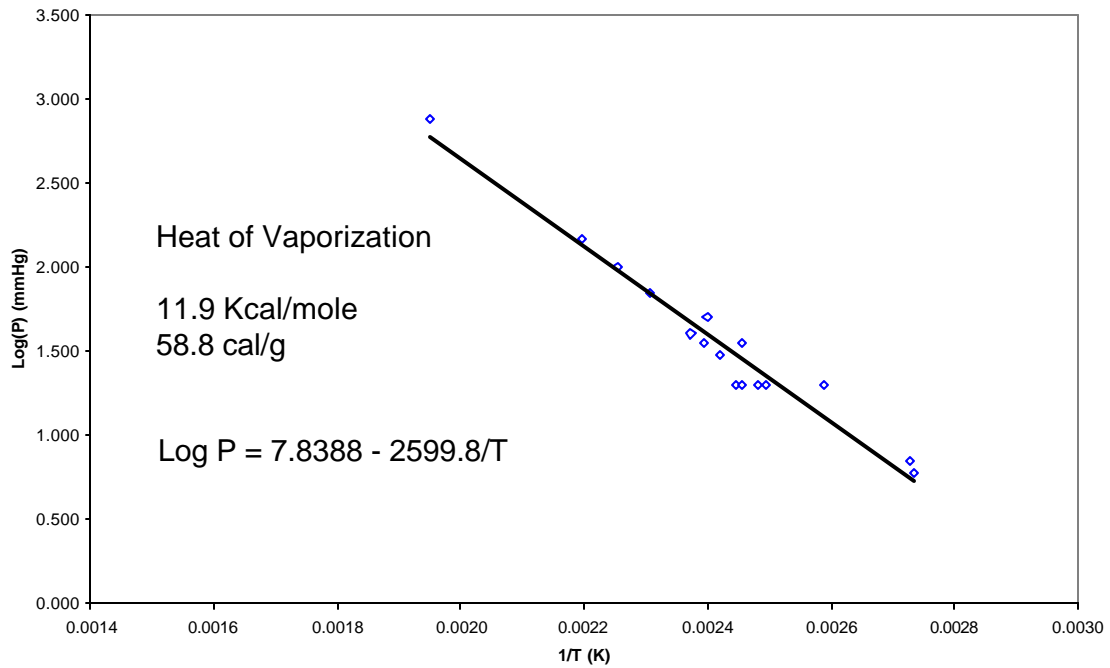


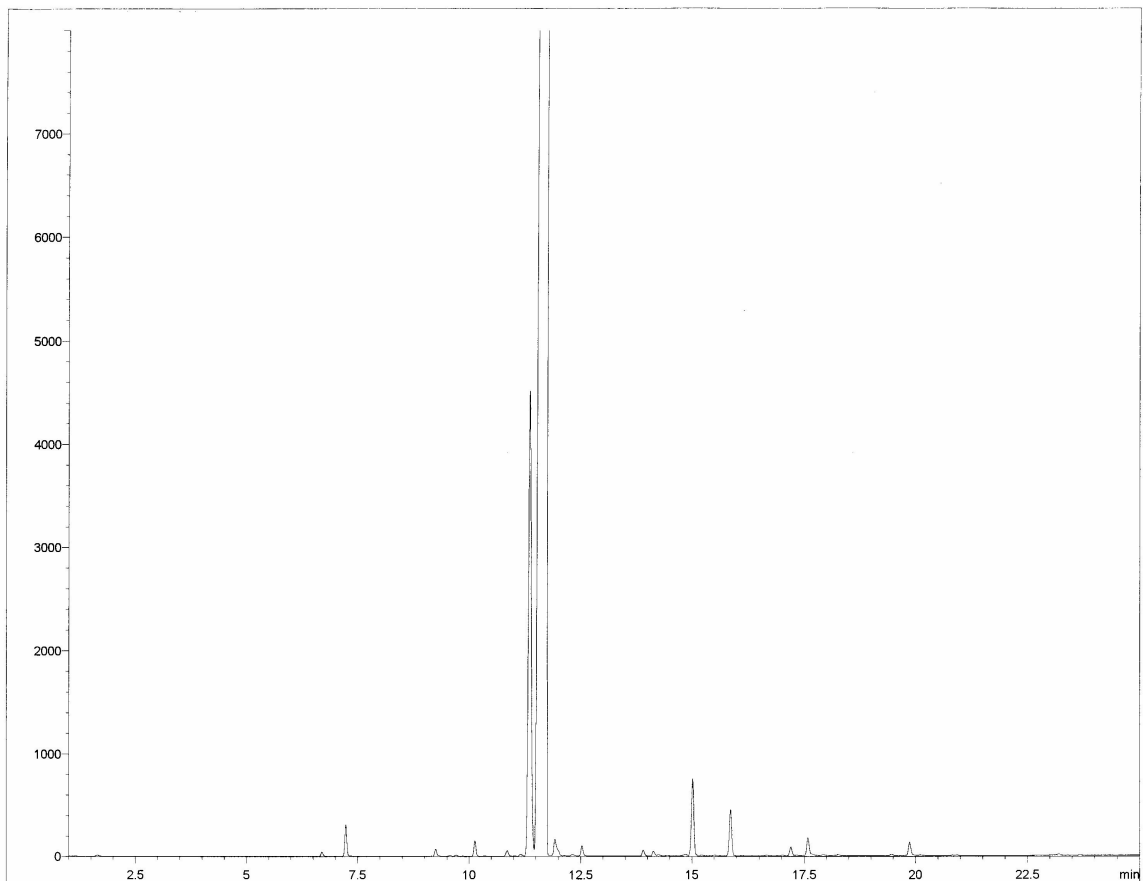
Figure 2:

**CYTOP 340 Vapor Pressure – Log P vs. 1/T**



**Figure 3**

**Typical CYTOP 340 GC Trace**



**Table 1**

**GC Retention Times of CYTOP 340 Components**

<u>Retention Time</u> <u>(min)</u>	<u>Component Identification</u>
1.7	mono-butylphosphine
7.2	di-butylphosphine
10.2	nitrile from initiator
11.3	di-butyl(sec-butyl)phosphine
11.7	tri-butylphosphine
15.1	di-butyl(2-ethylhexyl)phosphine
15.8	tri-butylphosphine oxide

Figure 4:

Typical **CYTOP 340**  $^{31}\text{P}$  NMR Spectrum

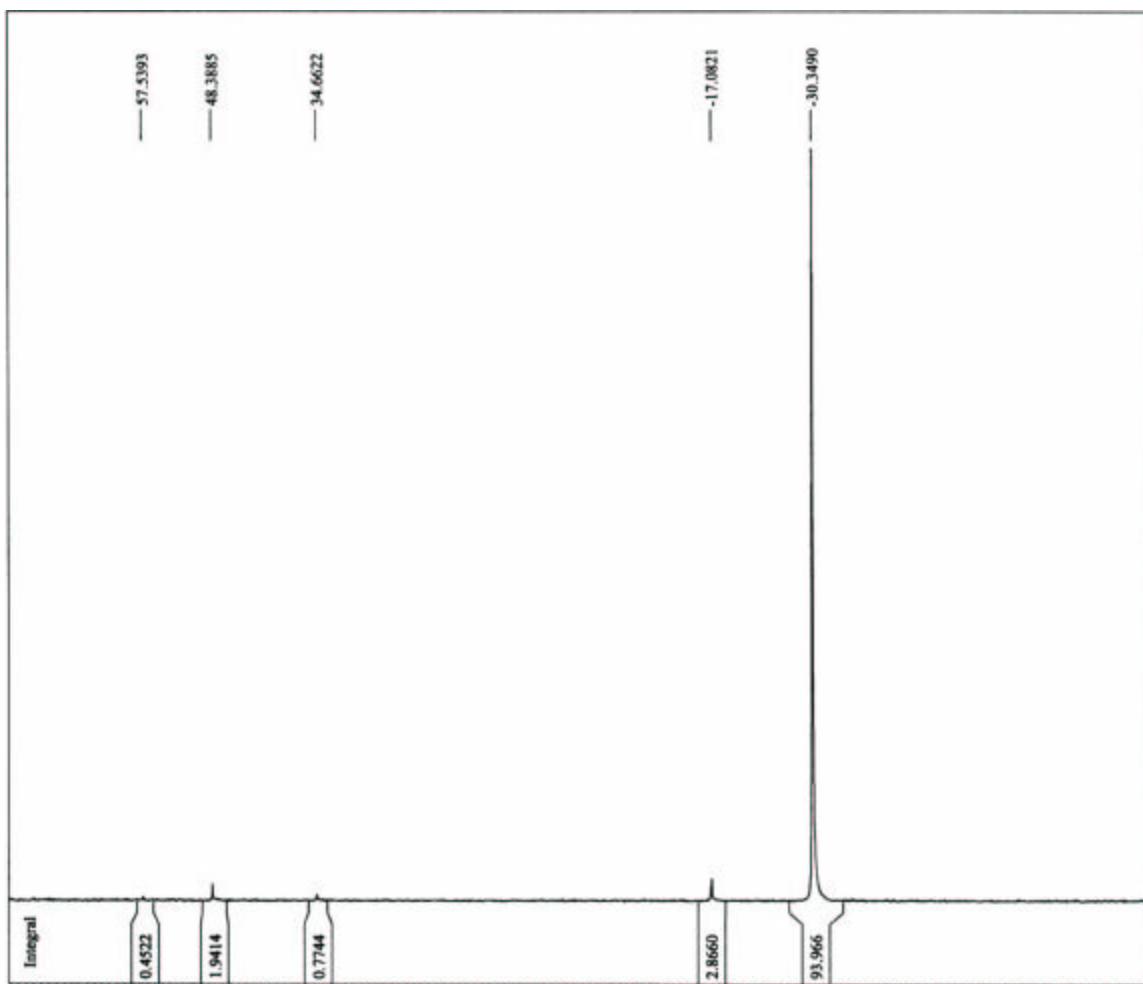


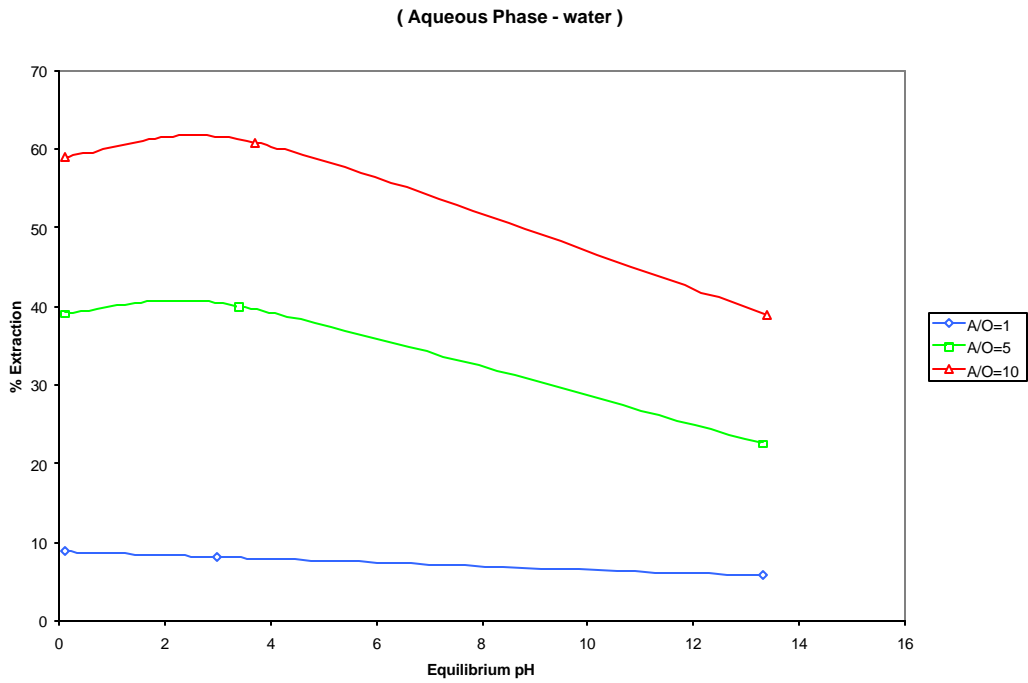
Table 2

Chemical Shifts of **CYTOP 340** Components

<u>Chemical Shift</u> (ppm)	<u>Component Identification</u>
-30.34 ppm	tributylphosphine
-17.08 ppm	dibutyl(sec-butyl)phosphine
+34.66 ppm	dibutyl(butyl)phosphonate
+48.38 ppm	tributylphosphineoxide

**Figure 5**

**Effect of the Aqueous pH on the Extraction of Tributylphosphine Oxide**



**Figure 6**

**Tributylphosphine Oxide Extraction Isotherm from Toluene**

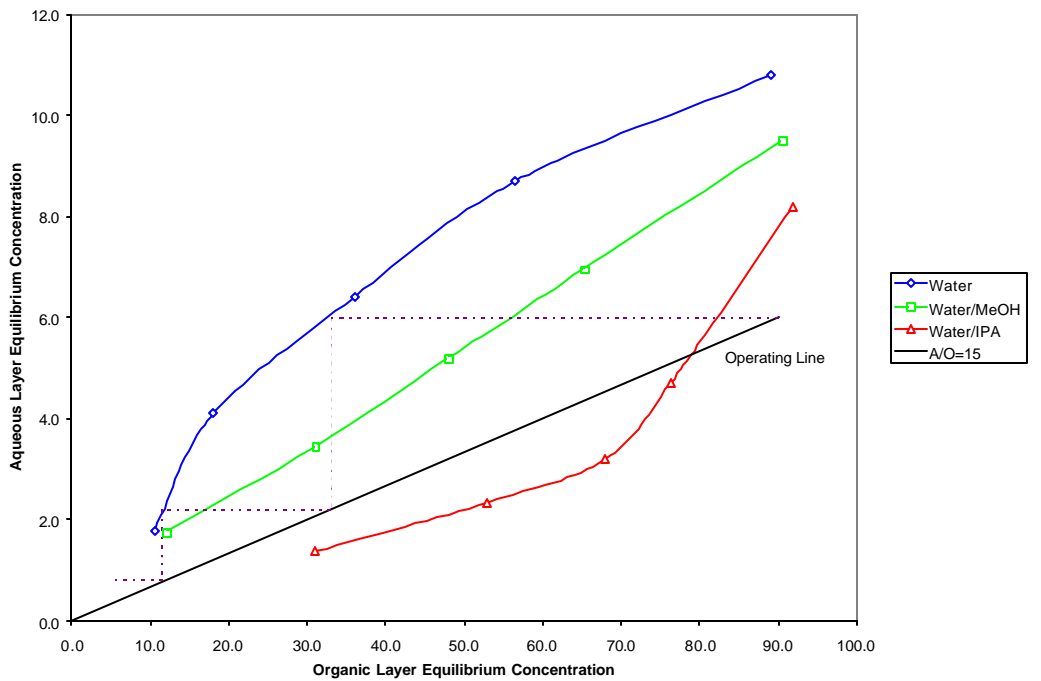
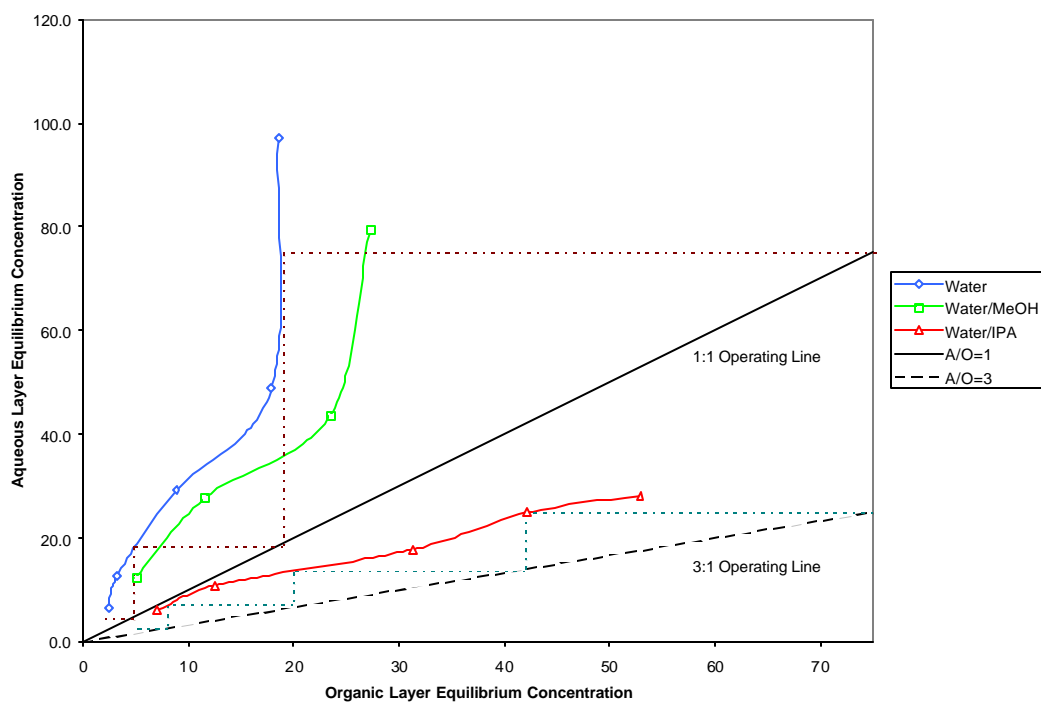


Figure 7

### Tributylphosphine Oxide Extraction Isotherm from Octane



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