ENCYCLOPEDIA

of

Reagents

for

Organic

Synthesis

Editor-in-Chief
Leo A. Paquette

Volume 8
Trip - Z
Indexes

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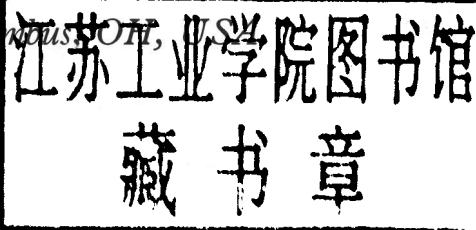
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The Ohio State University, Columbus, OH, USA

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Preface

The extent to which organic synthetic methodology has developed and flourished during the past several decades has placed unusually heavy demands on the broad range of scientists who utilize chemical reagents. There exists the vital need to know which reagent will perform a specific transformation. Since a number of reagents are often amenable to similar objectives, a researcher's ability to access readily a comparative summary of those features that distinguish one reagent from another can result in a considerable economy of time. The purpose of the *Encyclopedia of Reagents for Organic Synthesis* is to incorporate into a single work a genuinely authoritative and systematic description of the utility of all reagents used in organic chemistry. Its comprehensiveness is further served by an unrivaled ease to locate any specific entry or topic.

These objectives have been met by inviting practicing chemists from throughout the world to provide specific contributions in their area of expertise. Furthermore, the masthead for each of the 3000 reagents provides valuable information concerning physical data, solubility, form supplied in, purification, and, where relevant, preparative methods. The CAS registry number, handling/storing information, and precautions will further serve potential users. The first literature reference in each entry provides reviews, if available, dealing with the subject reagent. The critical coverage of all relevant literature is extensive.

The goal of the *Encyclopedia of Reagents for Organic Synthesis* is to serve as a reference work where the retrievability of useful information concerning any specific reagent is made facile. For this reason there is a detailed subject index and, in addition, a formula index of all the reagents, and also two further indexes that list the reagents by structural class and by function.

In any undertaking of this type, it is important that the term 'reagent' be clearly defined. The guideline that has dominated the thinking of the members of the Editorial Board is that a reagent be an agent or a combination of agents which with some generality effects the transformation of a substrate into a product. In addition, many useful building blocks have been included. As a consequence, we anticipate that a work has been produced that will serve biochemists, material scientists, pharmacologists, and chemical engineers, in addition to chemists from all disciplines, in that manner most conducive to accelerating progress in their respective fields of research.

The entries highlight the various uses characteristic of each reagent, with specific examples illustrative of these chemical reactions. The contributions are organized alphabetically and the cross-referencing to other reagents is liberal. Thus, a concerted effort has been made to bring together in one place a detailed compilation of the uses of those reagents that will serve both the beginning and experienced investigator. The wealth of facts contained within the *Encyclopedia of Reagents for Organic Synthesis* has been assimilated in a manner which will cause all scientists to want this source of information kept in close proximity to their laboratory.

A work of this magnitude could not have been brought to realization without the input of a great deal of time, effort, and dedication on the part of a large number of highly responsible individuals. I am especially indebted to the editors – Steven Burke, Robert Coates, Rick Danheiser, Scott Denmark, David Hart, Lanny Liebeskind, Dennis Liotta, Anthony Pearson, Hans Reich, James Rigby, and William Roush – for their tremendously valuable enthusiasm, intensive work, and unstinting persistence. A most critical role has been played by Colin Drayton, not only in conceiving the project but also as a consequence of his range of knowledge of the publishing business in steering us continually in the proper direction and in overseeing the massive editing operation. James Edwards and Mark Volmer are also to be thanked for their central role as assistant section editors. The body of this encyclopedia was composed by over 1000 authors from 40 countries around the world. The knowledge and expertise contributed by these experienced investigators in the form of authoritative treatises dealing with reagents with which they are thoroughly familiar constitutes the scientific underpinning of the entire undertaking. The enlightening end product of their contributions will have a major impact on the conduct of research in organic chemistry and I thank each of these individuals for their insightful entries.

The large contingent of organic chemists alluded to above, directly and indirectly, expects the *Encyclopedia of Reagents for Organic Synthesis* to play a vital role in stimulating creative research in organic chemistry in the years immediately ahead. All of us hope that you will share in this excitement by perusing its many pages and creatively adapting the valuable information contained therein.

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Foreword

This Encyclopedia covers comprehensively over 3000 reagents, alphabetically arranged using IUPAC nomenclature. The articles are self-contained but ***Bold Italics*** are used within each article to indicate other reagents that have their own entries in the Encyclopedia. A list of related reagents is given at the end of articles.

Although most articles are devoted to a single reagent, in some cases closely related reagents are covered under one heading, e.g. Methyl Trimethylsilylacetate is discussed in the article on Ethyl Trimethylsilylacetate, and Lithium Trimethoxyaluminum Hydride in the article on Lithium Tri-*t*-butoxyaluminum Hydride.

A particular reagent can be found either directly, by going to the appropriate place in the Encyclopedia, or from the Subject Index in Volume 8. Numerous other topics, such as types of reaction, named reactions, named reagents, general substrates or products, and specific substrates or products, are included in this index.

Volume 8 also contains a Formula Index, listing all reagents covered in the Encyclopedia.

In addition, there are two further compilations of all the reagents in Volume 8, a Reagent Structural Class Index and a Reagent Function Index. The former groups the reagents under headings such as Dienes, Hydrides, and Titanium Reagents, while the latter has headings such as Alkylating Agents, Desilylation Reagents, and Ring Expansion Agents.

The abbreviations used for journals in the references are on the front endpapers of all volumes, while the back endpapers list other abbreviations used throughout the Encyclopedia.

Trip

Triphenylacetonitrile *N*-Oxide

$$Ph_3C-C\equiv\overset{+}{N}-O^-$$
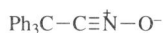
[13412-55-0]   C$_{20}$H$_{15}$NO   (MW 285.36)

(1,3-dipolar reagent[1])

Physical Data: mp 152–153 °C.[2]
Solubility: sol benzene, dioxane.
Form Supplied in: colorless solid; not commercially available.
Analysis of Reagent Purity: IR 2280, 1320 cm^{-1}; the corresponding isocyanate, the primary decomposition product, has a strong band at 2250 cm^{-1}.
Preparative Methods: usually prepared[2,3] by treatment of silver fulminate with triphenylmethyl chloride. The compound is reported[4] to be readily available from triphenylacetaldehyde oxime by treatment with bromine in an NaOH/H$_2$O/CCl$_4$ mixture at 0 °C, but no experimental details are provided.
Purification: recrystallization from a minimum amount of benzene.
Handling, Storage, and Precautions: if the reagent is being prepared from silver fulminate, extreme caution should be exercised due to the shock sensitivity. Unlike other nitrile oxides, which are usually generated in situ, triphenylacetonitrile oxide is a fairly stable solid. Upon heating it rearranges to triphenylmethyl isocyanate. Introducing a 3- or 4-trifluoromethyl group dramatically increases the proclivity towards rearrangement.[2]
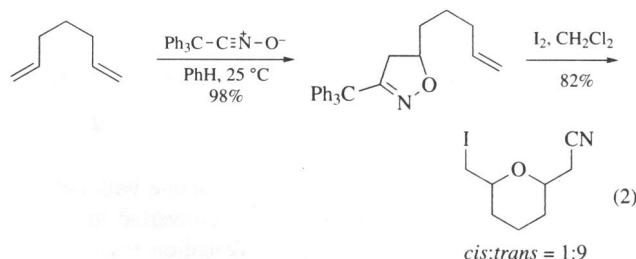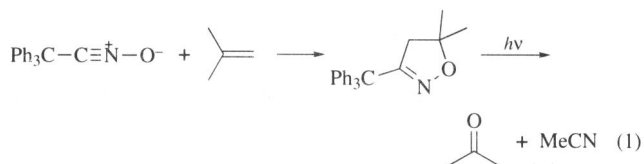

1,3-Dipolar Cycloaddition. Like other nitrile oxides (see *Acetonitrile N-Oxide*) this reagent is useful for 1,3-dipolar cycloaddition reactions. Alkenes give 3-triphenylmethyl-Δ^2-isoxazolines containing a labile Ph$_3$C group which may be used to trigger other events. For example, photolysis of 3-triphenylmethyl-Δ^2-isoxazolines fragments the heterocycle, presumably by homolysis of the Ph$_3$C–C bond (eq 1).[4] The triphenylmethyl group of 3-triphenylmethyl-Δ^2-isoxazolines is also the key to a novel preparation of cyclic ethers (eq 2).[5] The regiochemistry of dipolar cycloadditions of nitrile oxides containing bulky substituents has been studied.[6]

$$Ph_3C-C\equiv\overset{+}{N}-O^- + \quad\diagup\!\!\!= \longrightarrow \quad \underset{Ph_3C}{\diagdown}\diagup \overset{hv}{\longrightarrow}$$

$$\diagup\!\!\diagdown\!\!=\!\!O \; + \; MeCN \quad (1)$$

Related Reagents. Acetonitrile *N*-Oxide; 1-Pyrroline 1-Oxide.

---

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Dallas K. Bates
Michigan Technological University, Houghton, MI, USA

Triphenylarsine[1]

$$Ph_3As$$

[603-32-7]   C$_{18}$H$_{15}$As   (MW 306.25)

(nucleophilic agent for the synthesis of arsonium salts, which undergo epoxidation or alkenation reactions; can be used as a ligand)

Physical Data: plates (EtOH), mp 60.5 °C; bp 360 °C, 232–234 °C/14 mmHg.
Solubility: insol H$_2$O, ethanol; sol ether, THF, acetonitrile, etc.
Form Supplied in: commercially available.
Preparative Method: prepared from arsenic trichloride, chlorobenzene, and powdered sodium in benzene under reflux.[2]
Handling, Storage, and Precautions: use in a fume hood.

Introduction. Arsonium ylides are more reactive than the corresponding phosphonium ylides since the 'covalent' canonical form (ylene form) makes a smaller contribution to the overall structure of arsonium ylides (eq 1) than to that of phos-

phonium ylides.[1] This has been supported by X-ray crystallography.[3]

$$Ph_3As=CR^1R^2 \longleftrightarrow Ph_3\overset{+}{A}s-\bar{C}R^1R^2 \qquad (1)$$
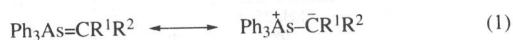
Arsonium Salts. Reaction of triphenylarsine with halo compounds forms arsonium salts which are converted to ylides on treatment with base. These perform alkenation reactions under PTC conditions.[4] A general procedure for the synthesis of unsaturated aldehydes, ketones, esters, and amides directly via arsonium salts in the presence of a weak base (solid **Potassium Carbonate**) under PTC conditions at rt has been devised (eq 2).[5] All the arsonium salts are stable and can be stored for a long time. The Ph$_3$AsO byproduct can be easily reconverted to Ph$_3$As by reduction.[6]

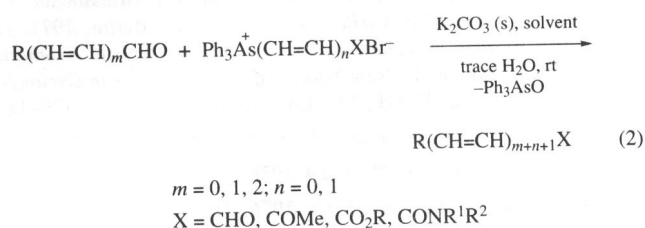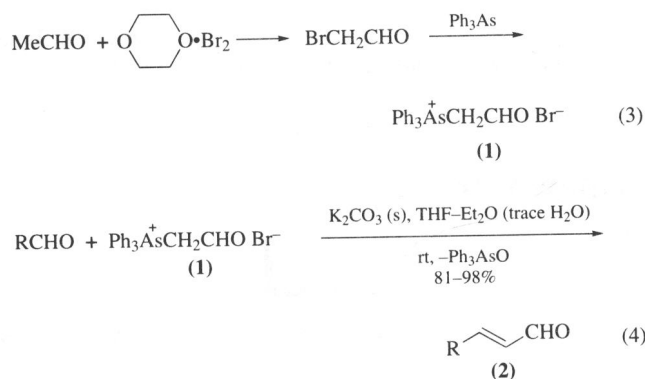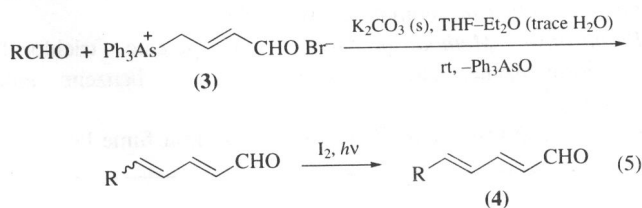$$R(CH=CH)_mCHO + Ph_3\overset{+}{A}s(CH=CH)_nXBr^- \xrightarrow[\substack{trace\ H_2O,\ rt \\ -Ph_3AsO}]{K_2CO_3\ (s),\ solvent}$$

$$R(CH=CH)_{m+n+1}X \qquad (2)$$

$$m = 0, 1, 2; n = 0, 1$$
$$X = CHO, COMe, CO_2R, CONR^1R^2$$

Formylmethyltriphenylarsonium bromide (**1**) (eq 3) reacts with aldehydes to give (E)-α,β-enals exclusively (eq 4).[7,8]

$$MeCHO + O\underset{}{\bigcirc}O\cdot Br_2 \longrightarrow BrCH_2CHO \xrightarrow{Ph_3As}$$

$$Ph_3\overset{+}{A}sCH_2CHO\ Br^- \qquad (3)$$
$$(1)$$

$$RCHO + Ph_3\overset{+}{A}sCH_2CHO\ Br^- \xrightarrow[\substack{rt,\ -Ph_3AsO \\ 81-98\%}]{K_2CO_3\ (s),\ THF-Et_2O\ (trace\ H_2O)}$$
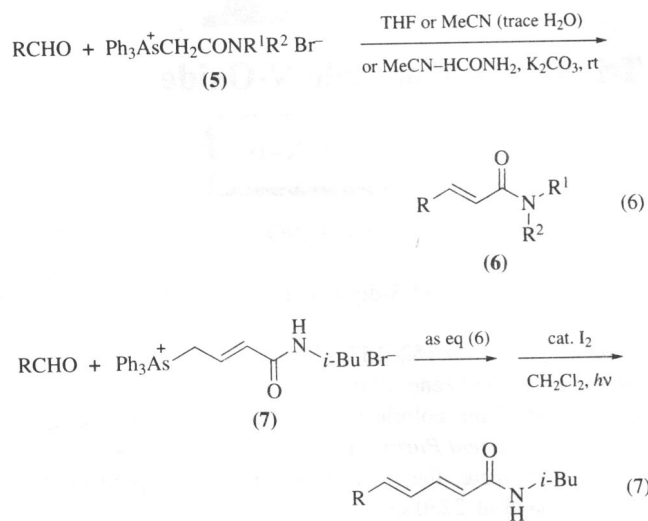$$(1)$$

$$R\diagup\!\!\diagdown\!\!^{CHO} \qquad (4)$$
$$(2)$$

Formylallyltriphenylarsonium bromide (**3**) reacts with aldehydes to give mixtures comprising mostly (2E,4E)- with some (2E,4Z)-dienals. The latter can be isomerized to the former by treating with a catalytic amount of **Iodine** in daylight (eq 5).[9]
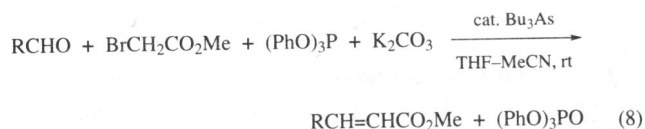
$$RCHO + Ph_3\overset{+}{A}s\diagup\!\!\diagdown\!\!\diagup^{CHO}\ Br^- \xrightarrow[\substack{rt,\ -Ph_3AsO}]{K_2CO_3\ (s),\ THF-Et_2O\ (trace\ H_2O)}$$
$$(3)$$

$$R\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown^{CHO} \xrightarrow{I_2,\ h\nu} R\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown^{CHO} \qquad (5)$$
$$(4)$$

2-(Oxoamido)triphenylarsonium bromides (**5**)[10] react with saturated and unsaturated aldehydes at rt in the presence of K$_2$CO$_3$(s) to afford (2E)-unsaturated amides (**6**) or (2E,4E)-

dienamides in excellent yields. No (Z) stereoisomer is detected (eq 6).[10] A vinylog (**7**)[11] reacts with aromatic aldehydes to give exclusively the (2E,4E)-products in 80–98% yield (eq 7); with aliphatic aldehydes, (2E,4E/2E,4Z) products are formed in a ratio of 85/15. The (2E,4Z) product can be isomerized to the (2E,4E) product.[11] The reactions of aldehydes with arsonium salts are listed in Table 1.

$$RCHO + Ph_3\overset{+}{A}sCH_2CONR^1R^2\ Br^- \xrightarrow[\substack{or\ MeCN-HCONH_2,\ K_2CO_3,\ rt}]{THF\ or\ MeCN\ (trace\ H_2O)}$$
$$(5)$$

$$R\diagup\!\!\diagdown\!\!\overset{\displaystyle O}{\underset{}{\diagup}}N\diagdown^{R^1}_{R^2} \qquad (6)$$
$$(6)$$

$$RCHO + Ph_3\overset{+}{A}s\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\overset{H}{\underset{O}{N}}\!\diagup^{i-Bu}\ Br^- \xrightarrow[\substack{}]{as\ eq\ (6)}$$
$$(7)$$

$$R\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\overset{\displaystyle O}{\underset{H}{N}}\!\diagup^{i-Bu} \xrightarrow{\substack{cat.\ I_2 \\ CH_2Cl_2,\ h\nu}}$$

$$R\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\overset{\displaystyle O}{\underset{H}{N}}\!\diagup^{i-Bu} \qquad (7)$$
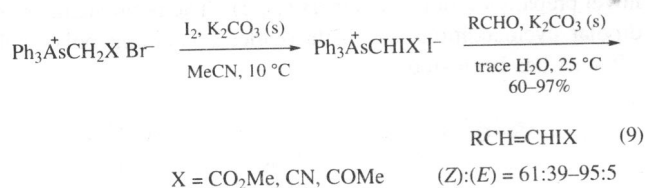
Triphenylarsonium salts have been used to synthesize a variety of natural products under very mild conditions: (E,Z)-diene sex pheromones,[12] pellitorine,[10b] trichonine,[13] *Achillea* amide,[10b] *Otanthus maritima* amide,[10a] (+)-yingzhaosu A,[14] LTA$_4$ methyl ester,[15] 19-hydroxy-LTB$_4$,[16] and lipoxins A$_4$ and B$_4$[17] have all been successfully synthesized.

Since tributylarsine is more reactive towards halides than triphenylarsine, Wittig-type alkenation of carbonyl compounds can be performed catalytically. Thus the reaction of various aldehydes with **Methyl Bromoacetate** (or **Bromoacetone**) in the presence of **Triphenyl Phosphite** and Bu$_3$As (0.2 equiv) provides α,β-unsaturated esters (or α,β-unsaturated ketones) in 60–87% yields and with (E)/(Z) ratios of 97:3–99:1 (eq 8).[18]

$$RCHO + BrCH_2CO_2Me + (PhO)_3P + K_2CO_3 \xrightarrow[\substack{THF-MeCN,\ rt}]{cat.\ Bu_3As}$$

$$RCH=CHCO_2Me + (PhO)_3PO \qquad (8)$$

An efficient one-pot synthesis of α-iodo- α,β-unsaturated esters, ketones, and nitriles via arsonium salts has been reported (eq 9).[19] A one-pot synthesis of *trans*-fluorovinylic epoxides has also been achieved (eq 10).[20]

$$Ph_3\overset{+}{A}sCH_2X\ Br^- \xrightarrow[\substack{MeCN,\ 10\ °C}]{I_2,\ K_2CO_3\ (s)} Ph_3\overset{+}{A}sCHIX\ I^- \xrightarrow[\substack{trace\ H_2O,\ 25\ °C \\ 60-97\%}]{RCHO,\ K_2CO_3\ (s)}$$

$$RCH=CHIX \qquad (9)$$

$$X = CO_2Me,\ CN,\ COMe \qquad (Z):(E) = 61:39-95:5$$

Silylated enynyl carboxylic esters can be synthesized with high stereoselectivity by the reaction of trimethylsilyl-2-

**Table 1** Reaction of Aldehydes (RCHO) with Arsonium Salts

Reagent		Mp (°C)	Product	Yield (%)	Ratio of isomer
$Ph_3\overset{+}{As}CH_2CHO\ Br^-$	(1)	160–161	RCH=CHCHO	81–98	only (E)
$Ph_3\overset{+}{As}CH_2CH=CHCHO\ Br^-$	(2)	153–154	RCH=CHCH=CHCHO	79–98	(2E,4E):(2E,4Z) = 1:1–4:1
	(5a)	191–192		81–98	only (E)
	(5b)	167–168		88–99	only (E)
$Ph_3As^+CH_2CONH\text{-}i\text{-}Bu\ Br^-$	(5c)	174–175	RCH=CHCONH-i-Bu	80–98	only (E)

$$(10)$$
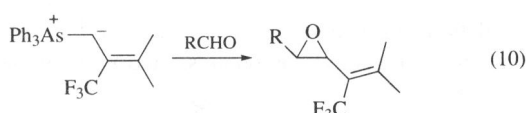
propynylidenetriphenylarsorane, prepared in situ from the corresponding arsonium salt with **n-Butyllithium**, and $BrCH_2CO_2R$ (eq 11).[21] Triphenylarsoranylideneketene reacts with 2-benzoylpyrrole in methylene chloride to give 1-phenylpyrrolizin-3-one in 85% yield (eq 12).[22]


$$(11)$$

$$(E):(Z) \approx 50:50$$

$$(12)$$
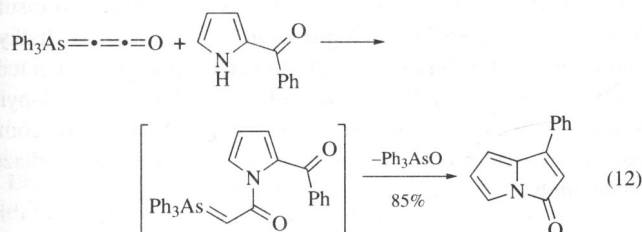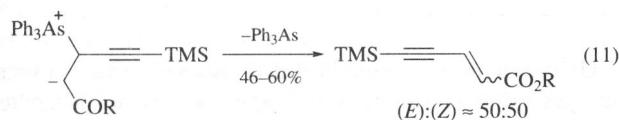
Methylenetriphenylarsorane ($Ph_3As=CH_2$), which is thermally unstable both in the solid state and in solution, has been isolated and characterized by analytical and spectroscopic methods.[23] Triphenylarsonium ethylide ($Ph_3As=CHCH_3$), prepared from triphenylethylarsonium tetrafluoroborate with **Potassium Hexamethyldisilazide** in THF/HMPT at –40 °C, reacts with aliphatic aldehydes to give *trans*-epoxides with high selectivity (eq 13). Stereoselection is lower with aromatic aldehydes (83% (E) for benzaldehyde). The reagent also reacts with ketones to form trisubstituted epoxides.[24]

$$(13)$$
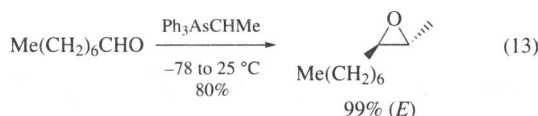
The synthesis and reactivity of (3,3-diisopropoxypropyl)triphenylarsonium ylide have been reported. This reagent can be considered as a β-formylvinyl anion equivalent (eq 14), as shown by the conversion of aldehydes to 4-hydroxy-2(E)-enals under very mild conditions (eq 15).[25] This route has been successfully applied to the total synthesis of (±)-hepoxilin A₃.[26]

$$(14)$$

$$(15)$$
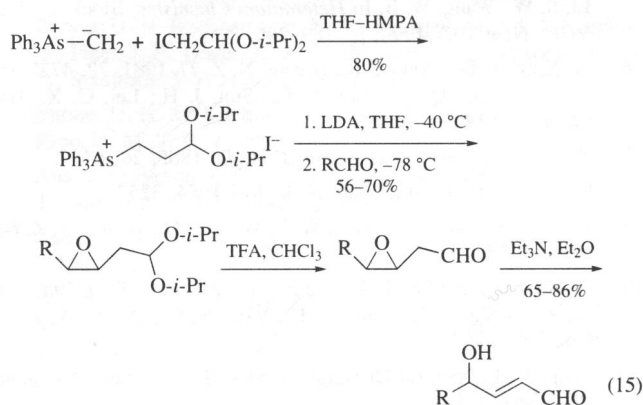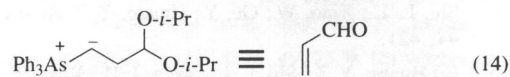
Homologation of aldehydes using (phenylthiomethylene)triphenylarsorane has been reported. Reaction with aldehydes gives exclusively α-phenylthio epoxides in THF and enol phenol thioethers in THF/HMPA. The former adducts are readily transformed to α-thiophenoxy carbonyl compounds and the latter to one-carbon homologated aldehydes (eq 16).[27]

$$(16)$$
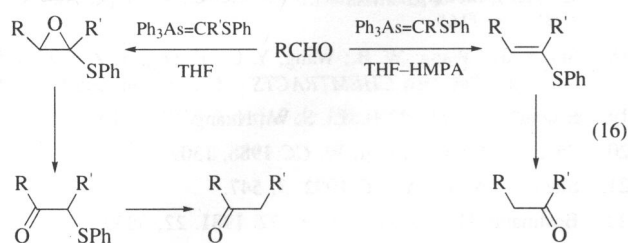
Large rate enhancement in Stille cross-coupling reactions is observed with triphenylarsine (a factor of 70 over the triphenyl phosphine-based catalyst) (eq 17).[28]

$$(17)$$
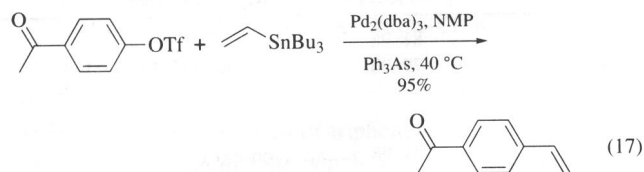
Related Reagents. Dibutyl Telluride; Tri-*n*-butylstibine; Triphenylphosphine.

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Triphenylbismuth Carbonate[1]

$$Ph_3BiCO_3$$

[47252-14-2] $C_{19}H_{15}BiO_3$ (MW 500.32)

(oxidation of alcohols; glycol cleavage;[4] *C*-phenylation of phenols,[3] carbonyl compounds,[7] and nitrogen derivatives[7])

Physical Data: mp 164 °C.[2]
Solubility: insoluble most organic solvents; reacts with carboxylic and sulfonic acids to give the corresponding diesters.
Preparative Method: prepared by reaction of **Triphenylbismuth Dichloride** with **Potassium Carbonate** in acetone–water.[3]
Handling, Storage, and Precautions: stable white powder; can be stored in the refrigerator for months. Use in a fume hood.

Oxidation of Alcohols.[4] Ph_3BiCO_3 is a very effective heterogeneous oxidant for primary, secondary, allylic, and benzylic alcohols, which are converted into the corresponding carbonyl derivatives under neutral conditions. Thiols are oxidized to disulfides, but the thiocarbonyl group in xanthates, *N,N*-dialkyl thionocarbamates, and di-*t*-butyl thioketone remain unaffected. Aniline, dimethylaniline, pyrrolidine, indole, and 3-pyrrolidinocholesta-3,5-diene are not oxidized. Hydrazo compounds are oxidized to azo compounds and hydrazones to diazo compounds.

Glycol Cleavage. Very high yields of carbonyl derivatives are obtained upon oxidation of 1,2-glycols with Ph_3BiCO_3.[4] As an example, the monobactam polyol in eq 1 is cleaved by Ph_3BiCO_3 to the disulfide in 85% yield.[5]

$$(1)$$
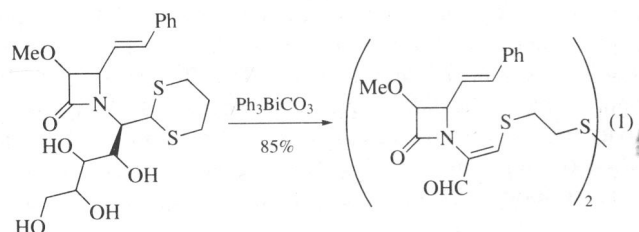
Phenylation.

Phenols.[3,6] The nature of the product of the reaction of Ph_3BiCO_3 with phenols is very dependent upon the nature of the phenolic substrate. Thus, whereas β-naphthol reacts in the pres-

ence of TMG to give α-phenyl-β-naphthol (76%) (eq 2), 2,6-dimethylphenol gives 2,2',6,6'-tetramethyldiphenoquinone (92%) (eq 3), and phloroglucinol is converted to a perphenyl enedione and a small amount of 2,4,6-triphenylphloroglucinol (eq 4).

$$\text{(2)}$$

$$\text{(3)}$$

$$\text{(4)}$$
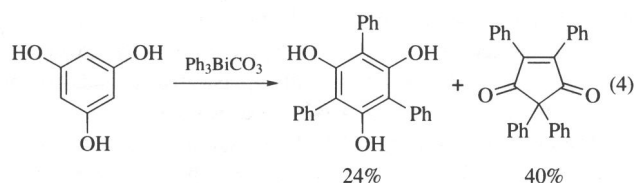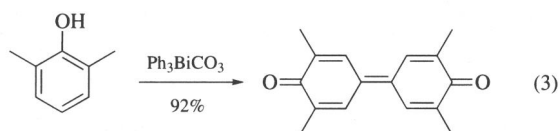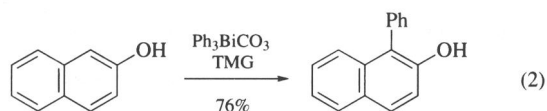
Carbonyl Compounds.[6,7] The arylation of ketones by Ar_3BiCO_3 (Ar = Ph, 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$) under basic cond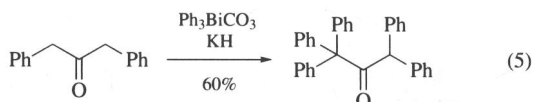itions leads to *C*-arylation of the carbons α to the carbonyl. When a THF solution of a ketone is treated with an excess of Ph$_3$BiCO$_3$ (2–8 equiv) in the presence of KH as base, the α,α'-perphenylated products are obtained in 60–93% yield (eq 5).

$$\text{(5)}$$

Enolic compounds, such as 1,3-dicarbonyl compounds, react with Ph$_3$BiCO$_3$ under neutral conditions to give the corresponding α-mono- or diphenyl derivatives. One major exception is dimedone, which affords a bismuthonium ylide instead of the 2,2-diphenylated compound. β-Keto sulfones also react easily with Ph$_3$BiCO$_3$ to afford the α-phenyl-β-keto sulfones;[8] this reaction can be used for a very efficient synthesis of isoflavanone and isoflavone derivatives. α-Arylglycine derivatives are obtained by the reaction of arylidene imines of glycine ethyl esters with Ar$_3$BiCO$_3$ under reflux in DMF (eq 6).[9] When the arylidene group is derived from *p*-chlorobenzaldehyde, a moderate yield of the diphenylated product is obtained, but selective monophenylation is realized with the benzophenone imine. This arylation procedure has also been extended to the synthesis of α-substituted α-phenylglycines.[10]

$$\text{(6)}$$

60% after hydrolysis
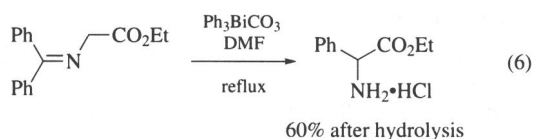
Nitrogen Derivatives. Ph$_3$BiCO$_3$ generally does not react with amines, but with *N*-phenylhydroxylamine it gives *N,N*-diphenylhydroxylamine.[11] Amides are reported to be *N*-phenylated in high yield.[12] Thus *N,N*-diphenylacetamide (90%) is obtained from the reaction of the sodium salt of acetamide with Ph$_3$BiCO$_3$; *N*-phenyl-*N*-methylbenzamide (90%) is obtained similarly from *N*-methylbenzamide. However, these results could not be repeated, although amides have been *N*-phenylated by ***Triphenylbismuth Dichloride*** in the presence of BTMG.[13] 2-Nitropropane reacts with Ph$_3$BiCO$_3$ under basic conditions (KH in THF) to afford α-nitrocumene in 80% yield.[7]

Triarylbismuth carbonates are highly efficient and selective reagents for the arylation of phenolic and enolic substrates. A useful though not so widely applicable class of reagents, which are complementary to the organobismuth reagents for the arylation of phenols and enols, are the aryllead triacetates.

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Triphenylbismuth Diacetate[1]

$$Ph_3Bi(OAc)_2$$
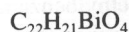
[7239-60-3] $C_{22}H_{21}BiO_4$ (MW 558.41)

(oxidation of alcohols and glycols;[3] *O*- and *N*-phenylation[9,14,16])

Physical Data: mp 187–189 °C.[2]
Solubility: sol CH_2Cl_2, $CHCl_3$; insol ether, MeOH.
Preparative Methods: prepared by treatment of ***Triphenylbismuth Carbonate*** with ***Acetic Acid*** in CH_2Cl_2,[3] or by ***Lead(IV) Acetate*** oxidation of ***Triphenylbismuthine***.[2a] The best yield (60%) is obtained by treatment of Ph_3Bi with $Pb(OAc)_4$ in AcOH for 2 h at rt, followed by addition of water, filtration, and recrystallization (CH_2Cl_2–ether).
Handling, Storage, and Precautions: stable white solid; can be stored under inert gas in the refrigerator for some months. Use in a fume hood.


Oxidation of Alcohols and 1,2-Glycols. Under basic conditions (either ***Potassium Carbonate*** or an organic base such as ***1,8-Diazabicyclo[5.4.0]undec-7-ene*** or ***1,1,3,3-Tetramethylguanidine***), this reagent oxidizes alcohols to the corresponding carbonyl compounds.[3,4] In a fashion similar to Ph_3BiCO_3, $Ph_3Bi(OAc)_2$ reacts with vicinal glycols in the presence of K_2CO_3[3] or with the stannylene derivatives of vicinal glycols[5] under neutral conditions to afford the two corresponding carbonyl fragments in high yield.

Phenylation of Alcohols. In the absence of base, $Ph_3Bi(OAc)_2$[6,7] and the related reagent $Ph_4BiOCOCF_3$[8] (prepared by reaction of Ph_5Bi with 1 equiv of CF_3CO_2H, mp 120–132 °C, $C_{26}H_{20}BiF_3O_2$, MW 630.44, *[83566-43-2]*) react with primary and secondary alcohols to afford mostly the corresponding *O*-phenyl ethers with various amounts of oxidation products. In the presence of a copper catalyst, 62–97% of the *O*-phenyl ethers can be obtained with simple alcohols and $Ph_3Bi(OAc)_2$ (eq 1). As copper catalyst, ***Copper(II) Chloride***, ***Copper(I) Chloride***, ***Copper(II) Acetate***, or metallic ***Copper*** can be used.[9]

$$ROH + Ph_3Bi(OAc)_2 \xrightarrow{CuX_n} R\text{–}O\text{–}Ph \quad (1)$$
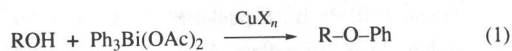
Miscellaneous Phenylation Reactions. In a very simple procedure, α-, β-, γ-, or δ-diols can be efficiently monophenylated by simple reflux of the diol and $Ph_3Bi(OAc)_2$ (1 equiv) in CH_2Cl_2 until disappearance of the diol (eq 2).[10] For secondary–tertiary diols, the secondary *O*-phenyl ethers are obtained, and for axial–equatorial diols, the axial ethers are obtained. With an excess of $Ph_3Bi(OAc)_2$, the bis-ether can be obtained.[9] Addition of a small amount of $Cu(OAc)_2$ (0.1 equiv or less) increases the reaction rate significantly, and the reaction can then be performed in a variety of solvents (eq 3).[9] Moreover, addition of

chiral pyridine oxazolines leads to a moderate optical induction in the case of the *meso-cis*-1,2-cyclohexanediol.[11]

$$(2)$$

$$(3)$$
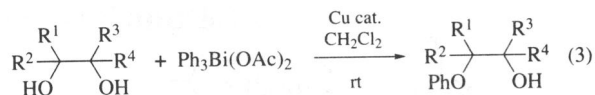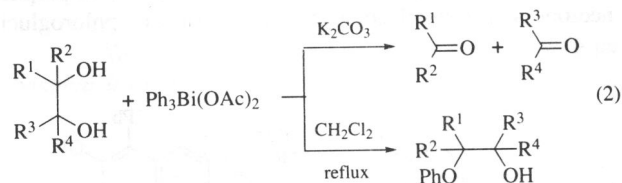
Whereas thiols are oxidized with Ph_3BiCO_3 or Ph_3BiCl_2 and base or $Ph_4BiOCOCF_3$ and base, they gave the corresponding phenyl thioether when treated with $Ph_4BiOCOCF_3$ under neutral or acidic conditions.[12] However, in the case of hydroxythiols, the copper-catalyzed reaction with $Ph_3Bi(OAc)_2$ leads to mixtures of mono- and di-*O*-phenylated disulfides.[9]

Phenols react with $Ph_4BiOCOCF_3$ (under neutral conditions or with acid catalysis) in benzene under reflux to afford moderate to good yields of the *O*-phenyl ethers.[13] Faster rates and better yields can be obtained through copper catalysis. However, $Ph_3Bi(OAc)_2$ under copper metal catalysis in CH_2Cl_2 at rt effects a more efficient and selective *O*-phenylation of electron-poor as well as electron-rich phenols (eq 4). Except for highly hindered phenols, such as 2,6-di-*t*-butylphenol, yields are generally high.[14]
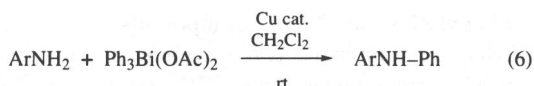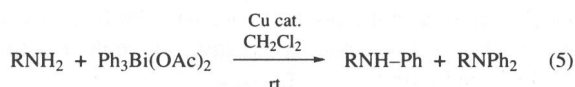
$$ArOH + Ph_3Bi(OAc)_2 \xrightarrow[\text{rt}]{\substack{\text{Cu cat.} \\ CH_2Cl_2}} ArO\text{–}Ph \quad (4)$$
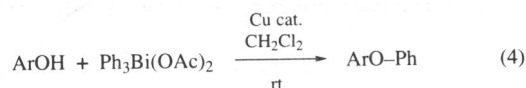
Enols are subject to mono-*O*-phenylation with $Ph_4BiOCOCF_3$ under neutral or, preferably, acidic conditions.[12] Copper catalysis leads to some improvement. Enols can also give the *O*-phenyl ethers by reaction with $Ph_3Bi(OAc)_2$ or the analogous reagent $Ph_3Bi(OCOCF_3)_2$ (prepared by action of CF_3CO_2H on Ph_3BiCO_3, mp 133 °C, $C_{22}H_{15}BiF_6O_4$, MW 666.35, *[83566-43-2]*) under copper metal catalysis. Yields are moderate to good.[14]

Phenylation of Amines. Under metallic copper catalysis, $Ph_3Bi(OAc)_2$ and $Ph_3Bi(OCOCF_3)_2$ react with aliphatic, heterocyclic, or aromatic amines in CH_2Cl_2 at rt to give the mono-*N*-phenyl derivatives in high yields (eq 5).[15,16] A number of α-amino acid esters are also selectively mono-*N*-phenylated under these conditions.[17] A wide range of variously substituted anilines have been mono- or di-*N*-phenylated with these reagents (eq 6). The most conveniently prepared reagent [$Ph_3Bi(OAc)_2$] is less reactive than $Ph_3Bi(OCOCF_3)_2$. Thus after 45 min, mesitylamine gives 40% of *N*-phenylmesitylamine with the former reagent, but 95% with the latter. Similarly, 4-nitroaniline gives 22% and 98%, respectively. Indoles are *N*- or *C*-3 phenylated only with $Ph_3Bi(OCOCF_3)_2$ under copper catalysis.[18]

The system $Ph_3Bi(OAc)_2$ + copper catalysis provides a broader spectrum of reactivity than the similar aryllead triacetates under copper catalysis, which do not effect phenol *O*-

$$RNH_2 + Ph_3Bi(OAc)_2 \xrightarrow[\text{rt}]{\substack{\text{Cu cat.} \\ CH_2Cl_2}} RNH-Ph + RNPh_2 \quad (5)$$

$$ArNH_2 + Ph_3Bi(OAc)_2 \xrightarrow[\text{rt}]{\substack{\text{Cu cat.} \\ CH_2Cl_2}} ArNH-Ph \quad (6)$$

arylation but which do react with anilines to give high yields of unsymmetrical diarylamines.[19]

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Triphenylbismuth Dichloride[1]

$$\boxed{Ph_3BiCl_2}$$

(Ph₃BiCl₂)
[594-30-9] $C_{18}H_{15}BiCl_2$ (MW 511.21)
(Ph₅Bi)
[3049-07-8] $C_{30}H_{25}Bi$ (MW 594.53)
(Ph₄BiOCOCF₃)
[83566-43-2] $C_{26}H_{20}BiF_3O_2$ (MW 630.44)
(Ph₄BiOTs)
[83566-44-3] $C_{31}H_{27}BiO_3S$ (MW 688.63)

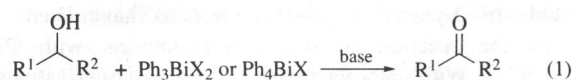(phenylation of phenols,[6] ketones and enols,[5] and nitro compounds[8])

Physical Data: mp 159–160 °C.[2]
*Solubility:* sol CH_2Cl_2, $CHCl_3$, benzene, toluene; insol ether, THF, MeOH.
Preparative Methods: easily prepared[2] by oxidation of **Triphenylbismuthine** either by bubbling **Chlorine** gas into an ethereal solution of Ph_3Bi at 0 °C, or by addition of 1 equiv of **Sulfuryl Chloride** to a solution of Ph_3Bi in CH_2Cl_2 at –78 °C. The action of **Phenyllithium** on Ph_3BiCl_2 leads to pentaphenylbismuth (mp 77–78 °C).[2] Addition of 1 equiv of a carboxylic or sulfonic acid to Ph_5Bi affords compounds of the type Ph_4BiX.[3] ($Ph_4BiOCOCF_3$: mp 120–132 °C; Ph_4BiOTs: mp 155–162 °C).
Handling, Storage, and Precautions: stable white solid; can be stored in the refrigerator in the absence of moisture. Pentaphenylbismuth is a poorly stable violet powder which can be stored under inert gas in the refrigerator for some days. $Ph_4BiOCOCF_3$ and Ph_4BiOTs are white powders which can be stored in the refrigerator under inert gas for some weeks. These reagents should be used in a fume hood.


Oxidation of Alcohols.[4] Treatment of primary or secondary alcohols with (a) Ph_3BiCl_2 or Ph_4BiX in the presence of a strong base (e.g. *1,1,3,3-Tetramethylguanidine*, BTMG (*t*-butyl-tetramethylguanidine), or *1,8-Diazabicyclo[5.4.0]undec-7-ene*) or with (b) Ph_5Bi under neutral conditions leads to oxidation to the corresponding carbonyl compounds under mild conditions in moderate to high yields (eq 1). Because of the similar reactivity patterns of these reagents, the system Ph_3BiCl_2 + base is the reagent of choice, due to its facile preparation and stability. An excess of reagent must be avoided, as possible side reactions such as α-*C*-phenylation can occur (see below).[5] The reaction of salts of tertiary alcohols, e.g. *t*-BuOLi, with Ph_3BiCl_2 results in the formation of the *O*-phenyl ethers e.g. *t*-BuOPh.[4c] In the presence of a base such as BTMG, Ph_3BiCl_2 cleaves glycols efficiently in the same way as Ph_3BiCO_3.

$$\underset{R^1 \quad R^2}{\overset{OH}{\diagup\!\!\diagdown}} + Ph_3BiX_2 \text{ or } Ph_4BiX \xrightarrow{\text{base}} \underset{R^1 \quad R^2}{\overset{O}{\diagup\!\!\diagdown}} \quad (1)$$

Phenylation of Phenols.[6] The reaction of phenols with organobismuth(V) reagents leads to a variety of products (eq 2). Phenols bearing electron-donating substituents react with Ph_3BiX_2 or Ph_4BiX in the presence of a strong base (BTMG, TMG, NaH, or KH) or with Ph_5Bi under neutral conditions to give mostly or only the *o*-mono- or *o,o'*-di-*C*-phenylated derivatives. With 2,6-disubstituted phenols, either 6-phenyl-6-methylcyclohexa-2,4-dienone or 4-phenyl-2,6-di-*t*-butylphenol are obtained, in contrast to the reaction with Ph_3BiCO_3 which gives diphenoquinones. Unactivated phenols or phenols bearing *meta* electron-withdrawing substituents afford mixtures of *O*- and *ortho*-*C*-phenylphenols. Phenols bearing *para* electron-withdrawing substituents give exclusively *O*-phenyl ethers after thermal decomposition of the aryloxybismuth intermediate. As these *O*-phenyl ethers can be obtained under milder conditions (neutral, rt) with **Triphenylbismuth Diacetate** under $Cu(OAc)_2$ catalysis, the present system does not compete efficiently.

$$\text{(2)}$$
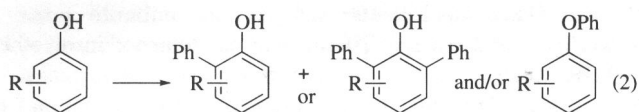
Phenylation of Ketones and Enolic Compounds.[5] In the presence of a strong base, ketones react with Ph_3BiCl_2 or Ph_4BiX to afford mostly or only the perphenylated derivatives. For example, cyclohexanone affords 2,2,6,6-tetraphenyl-cyclohexanone in 80% yield with $Ph_4BiOTs + KH$.[7] Ph_5Bi does not react with nonenolizable ketones, but with enolizable ketones the reaction does take place. Thus 2-phenylethanol is oxidized by Ph_5Bi and the aldehyde further reacts to afford, eventually, triphenylacetaldehyde in 69% yield.[5] Enolizable compounds such as β-dicarbonyl derivatives react with Ph_5Bi under neutral conditions, or with Ph_3BiCl_2 and Ph_4BiX (both in the presence of a strong base), to afford generally the α-perphenylated derivatives. For example, this reaction occurs with acetylacetone, ethyl acetoacetate, ethyl cyclohexanone-2-carboxylate (eq 3), ethyl cyclopentanone-2-carboxylate, diethyl malonate, and dimedone.[5,8]

Ph_5Bi	57%
Ph_3BiCl_2, BTMG	75%
$Ph_4BiOCOCF_3$, BTMG	91%

$$\text{(3)}$$
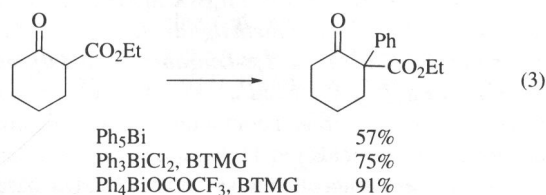
With acetylacetone, Ph_3BiCl_2 and base leads to 3,3-diphenylacetylacetone (74%), whereas $Ph_4BiOCOCF_3$ in benzene under reflux in the absence of base gives a moderate yield of the 3-monophenyl derivative (34%). In the case of dimedone and Meldrum's acid, the reaction of their sodium salts with Ph_3BiCl_2 leads only to the stable crystalline bismuthonium ylides.[9] In an application in natural products chemistry, high yields of 3-phenyl-4-hydroxycoumarins have been obtained from the reaction of 4-hydroxycoumarins with Ph_5Bi at −23 °C.[10] With caprolactam-type malonic derivatives, completely different results are observed, depending on the reagent used. Thus 3-cyano-ε-caprolactam reacts only with Ph_5Bi to give 74% of 3-cyano-3-phenyl-ε-caprolactam; 3-ethoxycarbonyl-ε-caprolactam does not react with Ph_5Bi and gives only the *N*-phenylcaprolactam derivative through reaction with Ph_3BiCl_2 and base.[11]

Phenylation of Nitro Compounds. In the presence of BTMG, 2-nitropropane reacts with Ph_3BiCl_2 or Ph_4BiOTs to produce α-nitrocumene (86 or 77% respectively).[8] The reaction using Ph_3BiCl_2 and TMG has been applied to the synthesis of α-methyl-α-phenylglycine via arylation of α-nitropropionic acid esters.[12]

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Triphenylbismuthine[1]

$$\boxed{Ph_3Bi}$$

[603-33-8] $C_{18}H_{15}Bi$ (MW 440.31)

(catalyst for glycol cleavage;[5] phenylating agent for alcohols[7] and amines;[8] source of phenyl radicals under photolytic conditions[4])

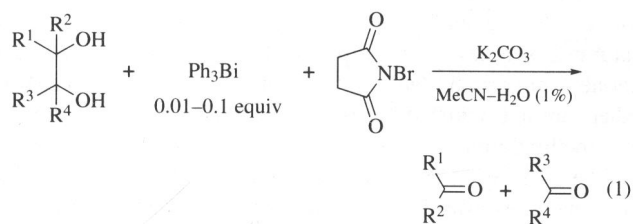*Alternate Name:* triphenylbismuth.
Physical Data: mp 77.6 °C.[2]
Solubility: CH_2Cl_2, $CHCl_3$, CCl_4, benzene, toluene, ether, THF, ethyl acetate; insol H_2O, alcohols; decomposed in acidic solvents.
Preparative Method: conveniently prepared by reaction of **Phenylmagnesium Bromide** with $BiCl_3$ in ether.[3]
Handling, Storage, and Precautions: must be stored in dark bottles in the absence of moisture or acidic vapors. Use in a fume hood.


α-Glycol Cleavage.[5] Triphenylbismuthine acts as a catalyst in the oxidative cleavage of α-glycols by **N-Bromosuccinimide** or **N-Bromoacetamide** in the presence of **Potassium Carbonate** to give the corresponding aldehydes and/or ketones. The oxidation is best performed by dropwise addition of an acetonitrile solution of NBS (4 equiv) to the mixture of the glycol, Ph_3Bi (0.01–0.1 equiv), and K_2CO_3 (4 equiv) in acetonitrile–water (99:1) in the dark at room temperature (eq 1). Yields are similar or better than those obtained with **Lead(IV) Acetate**, periodic acid and its salts, or the stoichiometric **Triphenylbismuth Carbonate** reagent. In contrast with these reagents, which cleave only *cis*-decalin-9,10-diol, the catalytic system cleaves both the *cis*- and the *trans*-decalin-9,10-diol isomers at nearly the same rate.


$$\begin{array}{c} R^1\ \ R^2 \\ R^3\ \ R^4 \\ OH\ \ OH \end{array} + \underset{0.01-0.1\ \text{equiv}}{Ph_3Bi} + \underset{}{NBr} \xrightarrow[\text{MeCN-H}_2\text{O (1\%)}]{K_2CO_3} \begin{array}{c} R^1 \\ R^2 \end{array}{=}O + \begin{array}{c} R^3 \\ R^4 \end{array}{=}O \quad (1)$$

Copper-Catalyzed Phenylations. Although there is no reaction between Ph_3Bi and **Copper(II) Acetate**, triphenylbismuthine can transfer a phenyl group to alcohols, phenols, or amines when a stoichiometric amount of copper diacylate is used.

Alcohols and phenols.[6,7] When primary or secondary alcohols are treated with Ph_3Bi in the presence of copper diacetate (Ph_3Bi:$Cu(OAc)_2$ = 1:2) without solvent in sealed ampules, the *O*-phenyl ethers are formed in 43–91% yields (based on the bismuth reagent) at a very slow rate (several days at rt) (eq 2). No

reaction with phenol has been described under these conditions. However, when a CH_2Cl_2 solution of 3,5-di-*t*-butylphenol is treated with a mixture of Ph_3Bi (1.2 equiv), $Cu(OAc)_2$ (2 equiv), and Et_3N (4 equiv), the corresponding *O*-phenyl ether is obtained in 44% yield after 10 h at rt. These *O*-phenylation reactions, particularly of phenols, are better performed with the more general copper-catalyzed **Triphenylbismuth Diacetate** system.

$$ROH + Ph_3Bi + Cu(OAc)_2 \xrightarrow{\text{neat}} R-O-Ph \quad (2)$$
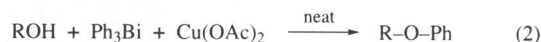
Amines.[7] Amines react smoothly at rt with Ph_3Bi (1.2 equiv) and $Cu(OAc)_2$ (0.5 equiv) to give high yields of *N*-mono- or *N,N*-diphenylated amines. Generally, monophenylated compounds are obtained with primary amines (eq 3) in variable yields, depending upon the basicity and steric hindrance of the substrate (6% for *p*-nitroaniline, 25% for mesitylamine, but 82% for *p*-methoxyaniline). With *n*-butylamine, the monophenyl (60%) and diphenyl (38%) derivatives are obtained. This reaction is less efficient than the related copper-catalyzed triphenylbismuth diacetate system. However, since Ph_3Bi is commercially available, this reaction is of interest for the monophenylation of anilines and a variety of aliphatic and heterocyclic amines.

$$RNH_2 + Ph_3Bi + Cu(OAc)_2 \xrightarrow[\text{rt}]{CH_2Cl_2} RNH-Ph \quad (3)$$
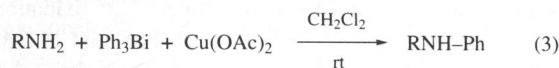
Palladium-Catalyzed Phenylation.[8] Triarylbismuthines Ar_3Bi (Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$) react with $Pd(OAc)_2$ (1 equiv) and **Triethylamine** (2 equiv) in HMPA to afford quantitatively the corresponding biaryl after heating for 10 min at 65 °C. When the reaction is performed in presence of acyl chlorides at 65 °C for 5 h in HMPA, phenyl ketones are obtained in 89–96% yields (eq 4). In the absence of the catalyst, phenyl ketones are also formed but in low yields.[9]

$$RCOCl + Ph_3Bi + Pd(OAc)_2 + Et_3N \xrightarrow[\text{65 °C}]{HMPA} RCO-Ph \quad (4)$$
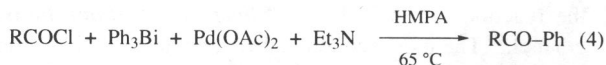
Other Uses. Triphenylbismuthine can also function as a catalyst or cocatalyst in the polymerization of hydrocarbons,[1c] and as a source of phenyl radicals under photolytic conditions.[4]

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Triphenylcarbenium Tetrafluoroborate

$$Ph_3C^+ \ BF_4^-$$
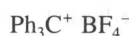
[341-02-6] $C_{19}H_{15}BF_4$ (MW 330.15)

(easily prepared[1] hydride abstractor used for conversion of dihydroaromatics to aromatics,[2-4] and the preparation of aromatic and benzylic cations;[5-8] oxidative hydrolysis of ketals[9] and thioketals;[10] conversion of acetonides to α-hydroxy ketones;[9] oxidation of acetals[11] and thioacetals;[12] selective oxidation of alcohols and ethers to ketones;[9,13-15] oxidation of silyl enol ethers to enones;[16] hydrolysis of TBS and MTM ethers;[17] oxidation of amines and amides to iminium salts;[18-20] oxidation of organometallics to give alkenes;[21-23] sensitizer for photooxidation using molecular oxygen;[24] Lewis acid catalyst for various reactions;[25] polymerization catalyst;[26] other reactions[27-30])

Alternate Name: trityl fluoroborate.
Physical Data: mp ~200 °C (dec).
Solubility: sol most standard organic solvents; reacts with some nucleophilic solvents.
*Form Supplied in:* yellow solid; commercially available.
Preparative Methods: the most convenient procedure involves the reaction of Ph₃CCl with **Silver(I) Tetrafluoroborate** in ethanol.[1b] The most economical route employs the reaction of Ph₃CCl with the anhydrous **Tetrafluoroboric Acid**–Et₂O complex.[1c]
Purification: recrystallization of commercial samples from a minimal amount of dry MeCN provides material of improved purity, but the recovery is poor.[1a]
Handling, Storage, and Precautions: moisture-sensitive and corrosive. Recrystallized reagent can be stored at rt for several months in a desiccator without significant decomposition. This compound is much less light-sensitive than other trityl salts such as the perchlorate.[1a]

Preparation of Aromatic Compounds via Dehydrogenation. Dihydroaromatic compounds are easily converted into the corresponding aromatic compound by treatment with triphenylcarbenium tetrafluoroborate followed by base.[2] Certain α,α-di-

substituted dihydroaromatics are converted to the 1,4-dialkylaromatic compounds with rearrangement (eq 1).[3] Nonbenzenoid aromatic systems, e.g. benzazulene[4a] or dibenzosesquifulvalene,[4b] are readily prepared from their dihydro counterparts. Aromatic cations are also easily prepared by hydride abstraction, for example, tropylium ion (e.g. in the synthesis of heptalene (eq 2)),[5] cyclopropenyl cation,[6] and others, including heterocyclic systems.[7] Some benzylic cations, especially ferrocenyl cations,[8] can also be formed by either hydride abstraction or trityl addition.

$$(1)$$

$$(2)$$
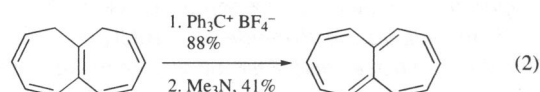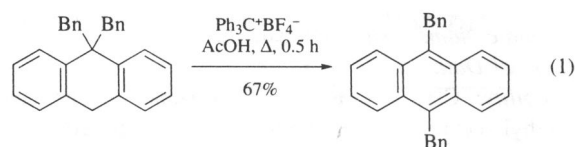
Oxidation by Hydride Abstraction. In the early 1970s, Barton developed a method for the oxidative hydrolysis of ketals to ketones, e.g. in the tetracycline series (eq 3).[9] The same conditions can also be used to hydrolyze thioketals.[10] Acetonides of 1,2-diols are oxidized to the α-hydroxy ketones in good yield by this reagent (eq 4).[9] The hydrogen of acetals is easily abstracted (eq 5), providing a method for the conversion of benzylidene units in sugars to the hydroxy benzoates.[11] The hydrogen of dithioacetals is also abstracted to give the salts.[12] Since benzylic hydrogens are readily abstracted, this is also a method for deprotection of benzyl ethers.[9,13] Trimethylsilyl, t-butyl, and trityl ethers of simple alcohols are oxidized to the corresponding ketones and aldehydes in good yield. Primary–secondary diols are selectively oxidized at the secondary center to give hydroxy ketones by this method (eq 6).[14] 2,2-Disubstituted 1,4-diols are oxidized only at the 4-position to give the corresponding lactones.[15] Trimethylsilyl enol ethers are oxidized to α,β-unsaturated ketones, thereby providing a method for ketone to enone conversion (eq 7).[16] t-Butyldimethylsilyl (TBDMS) ethers are not oxidized but rather hydrolyzed to the alcohols, as are methylthiomethyl (MTM) ethers.[17] Benzylic amines and amides can be oxidized to the iminium salts,[18] allylic amines and enamines afford eniminium salts,[19] and orthoamides give triaminocarbocations.[20]

$$(3)$$

$$(4)$$