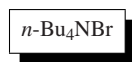


Tetrabutylammonium Bromide¹



[1643-19-2] C₁₆H₃₆BrN (MW 322.43)
 InChI = 1/C16H36N.BrH/c1-5-9-13-17(14-10-6-2,15-11-7-3)16-12-8-4;/h5-16H2,1-4H3;1H/q+1;/p-1/fC16H36N.Br/h;1h/qm;-1
 InChIKey = JRMUNVKIHC0MHV-SLKHSEMMCI

(phase-transfer catalyst;¹ source of nucleophilic bromide;¹ additive in transition metal catalyzed carbon–carbon bond-forming reactions;³¹ ionic liquid solvent³²)

Alternate Name: TBAB.

Physical Data: mp 103–104 °C.

Solubility: sol H₂O, 1% aq NaOH, CH₂Cl₂, EtOH; slightly sol toluene; insol 20% aq NaOH.

Form Supplied in: anhydrous white solid.

Analysis of Reagent Purity: tetraalkylammonium salts can be titrated with potassium 3,5-di-*t*-butyl-2-hydroxybenzenesulfonate and iron(III) chloride.^{1a}

Preparative Methods: several methods are available to recover the quaternary ammonium ion efficiently.^{1a} Prepared by reaction of tri-*n*-butylamine and *n*-butyl bromide.^{1a}

Purification: all manipulations should be carried out in a dry-box. The salt can be crystallized from benzene (5 mL g⁻¹) at 80 °C by adding 3 vol of hot hexane and allowing to cool. It can also be purified by precipitation of a saturated solution in dry CCl₄ by addition of cyclohexane or by crystallization from a mixture CH₂Cl₂–Et₂O. After filtration, the solid is further dried by heating at 75 °C under vacuo (0.1 mmHg) in the presence of P₂O₅.²

Handling, Storage, and Precautions: stable, highly hygroscopic; if used in a reaction requiring anhydrous conditions, it should be manipulated in a glove-bag or in a dry-box. Protect from moisture. Harmful by inhalation or ingestion.

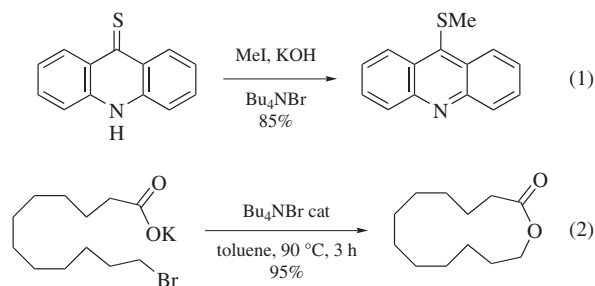
Original Commentary

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Catalyst for C–X Bond Formation. Tetrabutylammonium bromide is undoubtedly one of the most widely used phase-transfer catalysts. It combines the lipophilicity required for an efficient phase-transfer catalyst with the hydrophilicity necessary for efficient catalyst recovery. It has been successfully used in the liquid–liquid or solid–liquid phase-transfer alkylation of the NH groups of anilines,³ amides,⁴ lactams,⁵ sulfonamides,⁶ and other nitrogen heterocyclic compounds.⁷ Sulfur⁸ and oxygen-containing functional groups⁹ can also be smoothly alkylated under phase-transfer conditions. Several *S*-alkylthioacridines have been prepared by liquid–liquid¹⁰ or solid–liquid¹¹ phase-transfer catalysis (eq 1).

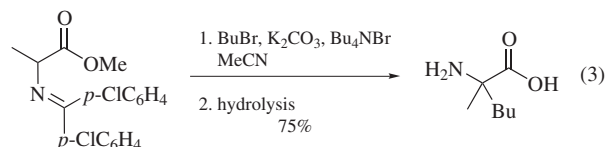
Carboxylic acids¹² and phenols¹³ can also be alkylated in the presence of tetrabutylammonium bromide. Macrolides can be synthesized by an intramolecular S_N2 reaction of a bromo ester via simulated high dilution conditions (eq 2).¹⁴



Bu₄NBr is also very effective in promoting nucleophilic aromatic substitution reactions to produce aryl thio esters,¹⁵ aryl ethers,¹⁶ and *N*-arylbenzodiazepines.¹⁷ Some glycosylations were shown to be efficient only in the presence of Bu₄NBr.¹⁸

Catalyst for Oxidation Reactions. Phase-transfer oxidation of alcohols to acids,¹⁹ alkenes to carboxylic acids,¹⁸ sulfides to sulfones,²⁰ and sulfilimines to sulfoximines²¹ have also been carried out in the presence of tetrabutylammonium bromide along with an oxidizing reagent.

Catalyst for C–C Bond Formation. The presence of Bu₄NBr was shown to be essential in a number of carbon–carbon bond-forming reactions, such as the alkylation of allyl sulfones²² and of *Malononitrile*,²³ and in the lead-promoted Barbier-type reaction of propargyl bromide with aldehydes.²⁴ It has also been used in the efficient synthesis of racemic α -alkyl and α,α -dialkyl α -amino acids by phase-transfer alkylation of Schiff bases (eq 3).²⁵



The presence of Bu₄NBr was shown to be necessary to increase the efficiency of some carbon–carbon double bond forming reactions such as Heck-type couplings,²⁶ dehydrohalogenations,²⁷ and Horner–Emmons–Wittig reactions.²⁸

Alkyl and Alkenyl Bromides. Bu₄NBr can be used as a powerful source of bromide for nucleophilic displacement reactions of triflates²⁹ and iodonium salts.³⁰

First Update

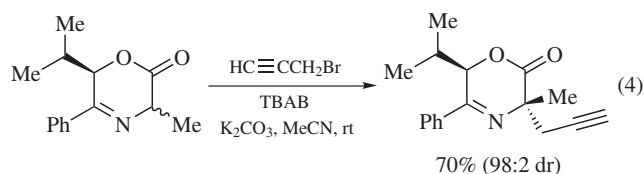
Rafael Chinchilla & Carmen Nájera

Universidad de Alicante, Alicante, Spain

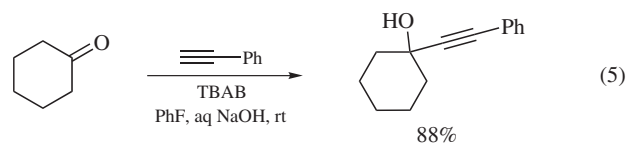
Phase-transfer Catalyst. TBAB is one of the most common phase-transfer (PT) catalysts, being employed in numerous C–C, C–N, C–O, C–S, and C–P bond forming reactions performed under liquid–liquid and liquid–solid phase-transfer catalysis (PTC) conditions, as well as in halogenation and oxidation reactions.³³

Substrates bearing acidic C–H hydrogens, easily removed under rather mild basic PTC conditions, are appropriate for C-alkylation reactions using TBAB as PT catalyst. *p*-Chlorophe-

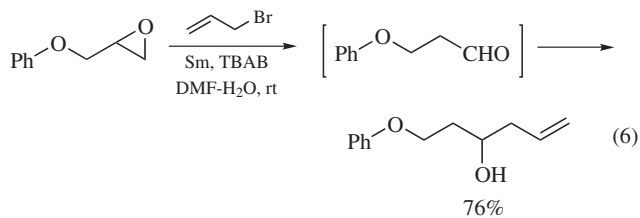
nylacetone nitrile is α -alkylated in the presence of TBAB under solid–liquid PTC conditions,³⁴ whereas 4-halobutyronitriles cyclizes to the corresponding cyclopropanes using a similar procedure.³⁵ Iminic derivatives of α -amino acids such as glycine³⁶ as well as cyclic derivatives of serine³⁷ are suitable substrates for alkylation reactions using TBAB under PTC conditions, driving to racemic mixtures of α -amino acid derivatives. When chiral derivatives are used as starting materials, diastereoselectively enriched C-alkylated compounds are obtained, leading to the asymmetric synthesis of amino acids. Chiral derivatives of glycine,³⁸ alanine³⁹ (eq 4),^{39a} or serine,⁴⁰ as well as peptides,⁴¹ are employed in these TBAB-promoted asymmetric alkylation reactions. Phosphonate equivalents of iminic glycinates react with acrylates in a Michael addition fashion under liquid–liquid PTC conditions in the presence of TBAB.⁴²



Aldehydes and ketones are alkynylated under liquid–liquid PTC conditions at room temperature yielding propargylic alcohols (eq 5), best results being obtained for aliphatic ketones and nonenolizable aldehydes.⁴³



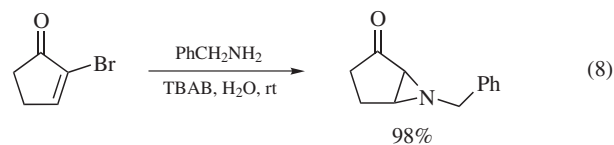
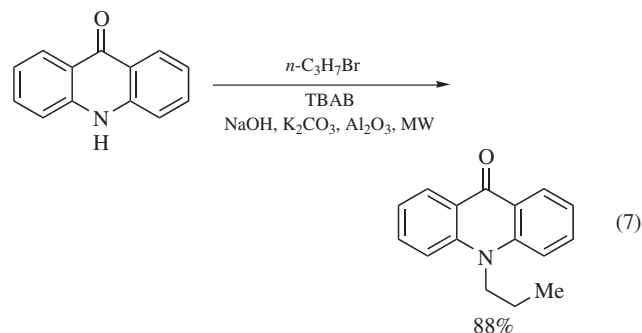
The use of TBAB as phase-transfer catalyst can be very effective in the creation of C–C bonds by using organometallic compounds that tolerate aqueous media. Tin in the presence of allyl bromides can be used for the allylation of aldehydes under Barbier conditions in water as solvent when using TBAB as catalyst.⁴⁴ Aldehydes are allylated using potassium allyl- and crotyltrifluoroborates in aqueous dichloromethane, the presence of TBAB significantly accelerating the reaction.⁴⁵ Samarium in the presence of allyl bromide can be used for the allylation of aldonitrone and hydrazones in aq DMF when TBAB is employed as an additive,⁴⁶ a reaction which can also be performed using gallium or bismuth.⁴⁷ Epoxides are coupled to allyl halides using gallium or samarium in aqueous media in the presence of a catalytic amount of TBAB to give homoallylic alcohols via preliminary epoxide rearrangement to the corresponding aldehyde (eq 6).⁴⁸



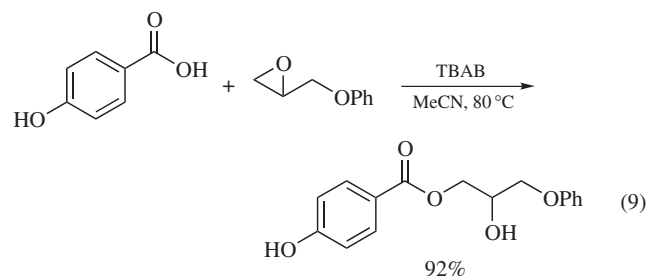
The role of TBAB in some of these reactions probably is not only that of phase-transfer catalyst, but also to activate the formed allylmetal reagents, as it is known that organolead compounds are activated with TBAB.²⁴ This activation ability is shown

in the coordination of the bromide anion of TBAB to neutral tin(IV) enolates, thus forming highly coordinated tin enolates with a marked change in chemoselectivity, showing low nucleophilicity toward carbonyl moieties and higher nucleophilicity to organic halides,^{49a} or high reactivity in Michael additions to α,β -unsaturated esters.^{49b}

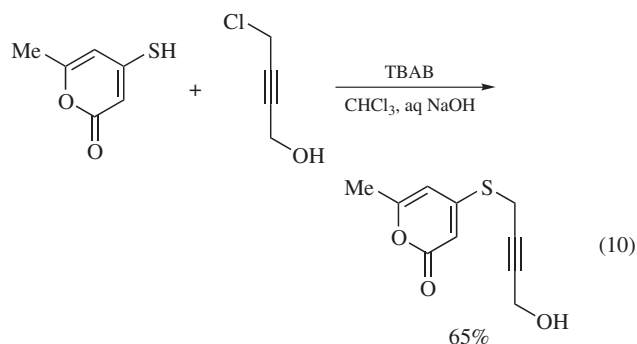
Imidazoles are *N*-alkylated at the 1-position using alkyl halides, an organic^{50a} or aqueous inorganic base,^{50b} and a catalytic amount of TBAB, conditions also suitable for the *N*-alkylation of carbazoles⁵¹ or quinoxalinones.⁵² Acridones are fast and efficiently *N*-alkylated when reacted with alkyl halides in a mixture of sodium hydroxide and potassium absorbed in alumina, in the presence of TBAB under microwave irradiation (eq 7).⁵³ The PTC conditions using TBAB as catalyst are used for the *N*-alkylation of sulfoximines,⁵⁴ *N*-diethoxyphosphoryl-*O*-benzylhydroxylamine⁵⁵ or amides, and lactams. In this last case solvent-free conditions and microwave irradiation accelerate considerably the reaction.⁵⁶ The aziridination of α -bromo-2-cyclopenten-2-one is performed using primary amines in water in the presence of TBAB (eq 8).⁵⁷



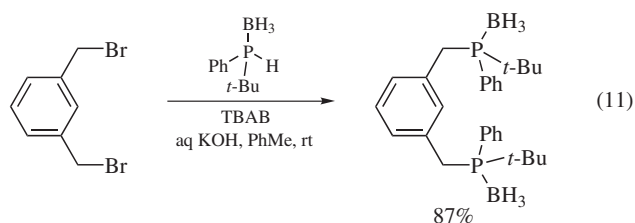
Alcohols can be alkylated in the presence of TBAB under liquid–liquid PTC conditions and an aqueous inorganic base.⁵⁸ The procedure is more easily performed when phenols are employed,⁵⁹ allowing solid–liquid⁶⁰ and solventless⁶¹ PTC reaction conditions. Monoesters of 1,2-diols are obtained from benzoic acid derivatives and epoxides by adding a catalytic amount of TBAB, the reaction not only involving a PT mechanism but also a stabilization of the dissociation of the benzoic acid and generation of hydrogen bromide which induces epoxide opening (eq 9).⁶² Carbonates are also obtained from chloroformates and phenols under solid–liquid PTC in the presence of TBAB.⁶³



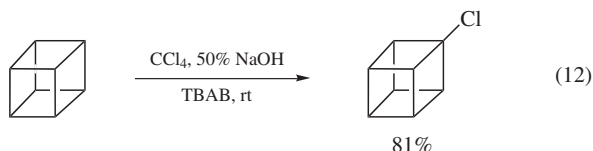
The *S*-alkylation of 4-mercapto-6-methyl-2-pyrone with allyl and propargyl halides is performed using TBAB as PT agent in chloroform-aqueous sodium hydroxide at room temperature (eq 10),⁶⁴ whereas the double alkylation of sodium sulfide can be carried out by mixing it with an alkyl halide under PTC conditions in a water–toluene mixture.⁶⁵



The *P*-alkylation of phosphane boranes can be carried out in an inorganic base-containing biphasic solution in the presence of TBAB as PT catalyst, which allows the synthesis of polydentate phosphane ligands in much higher yields than when using the *n*-butyllithium-promoted standard conditions (eq 11).⁶⁶

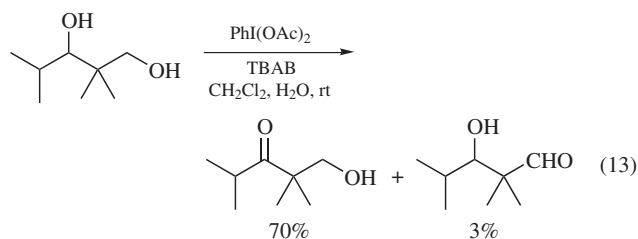


The monochlorination of cubane has been achieved using carbon tetrachloride in 50% aqueous sodium hydroxide in the presence of TBAB under PTC conditions,⁶⁷ the reaction probably involving SET from the hydroxide to carbon tetrachloride (eq 12). Chlorination of 2,3,5,6-tetrachloropyridine to pentachloropyridine can be achieved via carbanionic intermediates using chloroform or hexachloroethane in aqueous sodium hydroxide in the presence of TBAB.^{68a} These reaction conditions can also be employed for the preparation of 3,3-dichlorobenzosultams.^{68b}



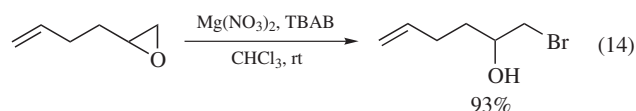
Benzylic carbons and the tertiary carbons in adamantanes are oxidized to alcohols and/or ketones by using molecular oxygen, *N*-hydroxyphthalimide as radical initiator, and TBAB.⁶⁹ Benzylic and allylic alcohols are oxidized to the corresponding aldehydes or ketones by using *tert*-butyl hydroperoxide in the presence of catalytic amounts of copper salts and TBAB as PT catalysts.⁷⁰ Oxone[®] in the presence of a manganese(III) complex as catalyst oxidizes secondary and benzylic alcohols to the corresponding carbonyl compounds under TBAB-promoted liquid–liquid PTC conditions,⁷¹ whereas *m*-CPBA is employed for the oxidation of alcohols in the presence of a catalytic amount of TEMPO and TBAB.⁷² Selective oxidation of secondary alcohols is achieved

using 2-iodoxybenzoic acid in the presence of TBAB under PTC conditions (eq 13).⁷³



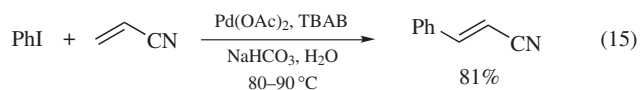
Methyl aryl ketones are converted into benzoic acids by using molecular oxygen and a catalytic amount of 1,3-dinitrobenzene under basic PTC reaction conditions promoted by TBAB.⁷⁴ Catalytic asymmetric epoxidation of *trans*-chalcone is achieved using basic hydrogen peroxide and poly-*L*-Leu as catalyst, the addition of TBAB significantly accelerating the reaction.⁷⁵

Source of Bromide. The use of TBAB as a source of the bromide anion allows the regioselective ring opening of epoxides to bromohydrins at room temperature when magnesium(II) nitrate is used as catalyst, the bromide attack taking place at the less-hindered position of the epoxide (eq 14).⁷⁶ This type of TBAB-promoted epoxide ring opening gives rise to five-membered cyclic orthoesters when performed in the presence of perfluorocarboxylates.⁷⁷ Cyclic sulfates from chiral 2,3-diol esters can also be regioselectively ring opened to bromohydrins for the synthesis of chiral α,β -epoxy esters.⁷⁸



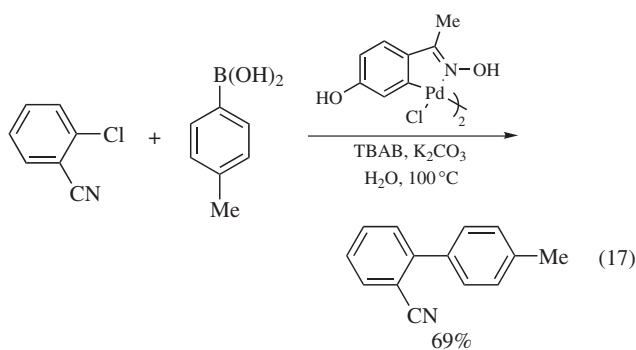
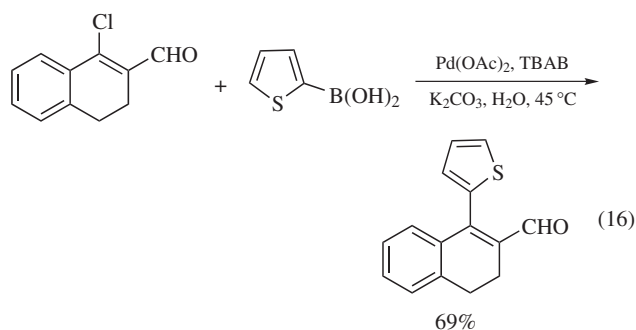
Hydroxyheteroarenes can be brominated by using a combination of phosphorus pentoxide and TBAB,⁷⁹ whereas diethyl α -hydroxyphosphonates can be transformed into the corresponding α -brominated derivatives by using a neutral system formed by triphenylphosphane and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in the presence of TBAB.⁸⁰

Additive in Transition Metal-catalyzed C–C Bond-formation Reactions. The addition of tetraalkylammonium salts frequently enhances the rate of transition-metal-catalyzed (mainly palladium) cross-coupling reactions, such as the Heck coupling,⁸¹ especially in aqueous solvents. Their effect cannot only be considered as a consequence of the typical phase-transfer activity, but also as a stabilization of nano-sized metal colloids that can be formed by reduction of the added metal source, the surfactant preventing undesired agglomeration to unreactive species such as palladium black by forming a monomolecular layer around the metal core.⁸² Thus, TBAB has been used as an additive in Heck cross-coupling reactions under ligand-free palladium catalysis⁸³ even in neat water⁸⁴ (eq 15), or using *N*-heterocyclic carbene palladium complexes⁸⁵ or CN-palladacycles⁸⁶ as palladium sources.



The addition of TBAB has also shown to enhance the rate of the palladium-catalyzed Suzuki cross-coupling reaction between

an aryl halide and an arylboronic acid [ArB(OH)₂] in aqueous solvents, not only by facilitating the solvation of the organic substrates and by stabilization of palladium nanoparticles, but also by the formation of [ArB(OH)₃]⁻[*n*-Bu₄N]⁺. Thus, when palladium(II) acetate is used as catalysts, TBAB accelerates the cross-coupling of iodoarenes,⁸⁷ bromoarenes,⁸⁷ chloroarenes,⁸⁸ bromothiophenes,⁸⁹ and β -chloroacroleins⁹⁰ (eq 16) in water, or the coupling of bromo or chloroarenes when using poly(ethylene glycol-400) as solvent.⁹¹ Oxime-derived palladacycles can be used as catalysts in the presence of TBAB in the Suzuki coupling of chloroarenes in water (eq 17),⁹² as well as di(2-pyridyl)methylamine-palladium dichloride complexes.⁹³

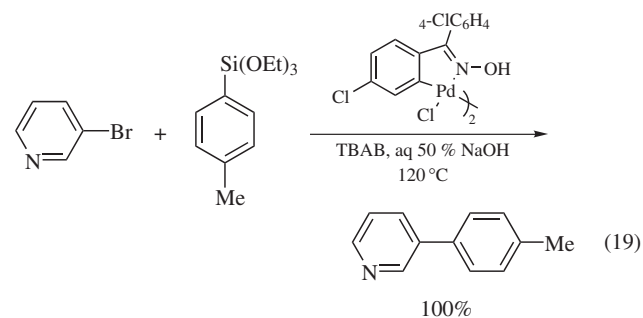
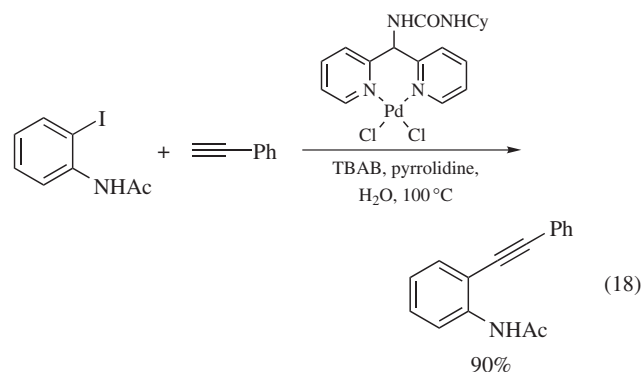


Recoverable nickel(0) metal colloids stabilized by the addition of TBAB catalyze the Suzuki coupling of aryl iodides and bromides with organoboronic acids using ethanol as solvent, the addition of triphenylphosphane being required when coupling activated aryl chlorides.⁹⁴

The addition of TBAB can promote the palladium-catalyzed Sonogashira coupling of aryl- or vinyl halides and terminal alkynes when using palladium(II) acetate as palladium source in ethanol as solvent⁹⁵ or palladium(II) chloride in water.⁹⁶ The use of TBAB as an additive has found to be particularly important when palladium-phosphinous acids⁹⁷ and di(2-pyridyl)methylamine-palladium dichloride complexes^{96a} (eq 18), even supported on a polymer,^{96b} have been used as catalysts in water as solvent.

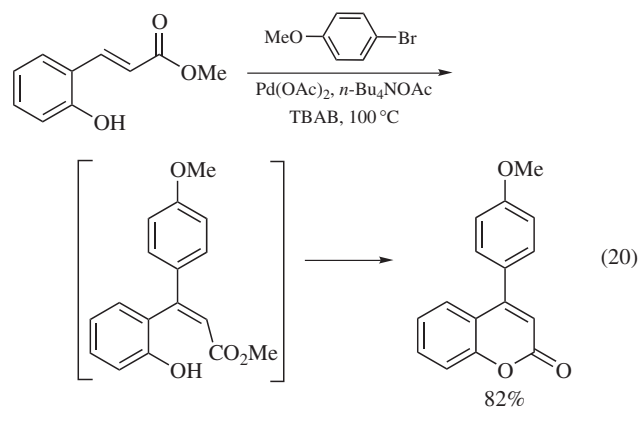
The use of TBAB as additive allows the solvent-less sodium hydroxide-promoted palladium-catalyzed Hiyama cross-coupling reaction of deactivated aryl bromides or -chlorides and arylsiloxanes, when palladium(II) acetate or an oxime-derived palladacycle (eq 19) are used as palladium sources.⁹⁸ The homocoupling of brominated or iodinated arenes to biaryls can be performed by

using the combination of palladium(II) acetate and TBAB in aq DMF,⁹⁹ as well as employing palladium on charcoal as palladium source and formate as reducing agent, in the presence of TBAB.¹⁰⁰



Ionic Liquid Solvent. Although the melting point of TBAB is slightly higher than 100 °C, which is the border temperature for considering a salt as an ionic liquid and not simply a molten salt,³² its melting temperature drops when other reagents are present; TBAB is therefore considered as an ionic liquid with all the recyclability advantages of such solvents.³² Molten TBAB has been used as a solvent in the Michael addition of thiols to electron-deficient olefins,¹⁰¹ the bismuth(III)-catalyzed ring opening of epoxides with anilines,¹⁰² the monobromination with *N*-bromosuccinimide of activated aromatics and heteroaromatics,¹⁰³ the cyclic carbonate formation from carbon dioxide and oxiranes,¹⁰⁴ and the transthioacetalisation of acetals.¹⁰⁵

The advantages of ionic liquids added to its transition metal nanoparticle stabilization ability, make molten TBAB applicable as solvent in cross-coupling reactions such as the palladium-catalyzed Heck reaction of aryl chlorides,^{106,107c} bromides,¹⁰⁷ or iodides,¹⁰⁸ the arylation of allylic alcohols,¹⁰⁹ and the synthesis of 4-arylated coumarins from *o*-hydroxycinnamates by a domino Heck reaction/cyclization process (eq 20).¹¹⁰ Nanoparticles created by reduction of palladium salts in nanoparticle-stabilizing molten TBAB can be used for the Suzuki cross-coupling reactions of aryl bromides or chlorides,¹¹¹ the carbonylation of aryl halides,¹¹² and the hydrogenolysis-free hydrogenation of olefins.¹¹³ Benzylic alcohols are dehydrogenated to the corresponding ketones in molten TBAB with a catalytic amount of palladium(II) chloride and a flow of argon.¹¹⁴



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