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## Phosphorous-based ionic liquids as condensing agent and medium for efficient esterification of carboxylic acids with alcohols and phenols

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### Abstract

*N*-(diphenylphosphino)triethyl- and tributylammonium salts are introduced as easily prepared, cheap and stable ionic liquids that act as the condensing agent and media for the efficient esterification of acids with alcohols and phenols. This class of ionic liquids is immiscible with the ester products and thus allows simple and easy separation of the desired products from the reaction mixture.

**Keywords:** *N*-(diphenylphosphino) triethylammonium; phosphorous ionic liquid; esterification; carboxylic acids; alcohols; phenols

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### 1. Introduction

Esterification of carboxylic acids is one of the most important functional group conversions in organic synthesis (Franklin, 1998 and 1999; Larock, 1999; Otera, 2003). The Fischer esterification is a reversible reaction which requires acid catalyst. The equilibrium is pushed to the product side by taking excess of a reactant and/or by continuously removing the water formed in the reaction. Sometimes it is necessary to employ an additional solvent to carry over the water in the form of azeotrope (Izumi et al., 1995; Okuhara et al., 1998; Otera et al., 1991). Such operations require large energy input to recycle the solvents and the excess reactants. The loss of volatile organic solvents to the atmosphere results in increases in the cost of production and also damage to the environment. To address the problem of chemical pollution, ionic liquids have received ever-increasing attention as environmentally friendly reaction media. They have favorable properties, such as non-volatility, non-flammability, nominal vapor pressure, remarkable thermal and chemical stability and superior electrical conductivity (Welton, 1999; Wilkes, 2002). A number of Brønsted acidic ionic liquids have been reported as catalyst and also medium in the esterification reactions. The majority of the ionic liquids reported for esterification are imidazole (Arfan and Bazureau, 2005; Cole et al.,

2002; Fraga-Dubreuil et al., 2002; Xing et al., 2005) and pyridine (Gui et al., 2004) derivatives most of which are synthesized in two or more steps using expensive materials. Herein, we report on the successful application of a new class of easily prepared, phosphorous-based, room-temperature ILs for acid-free esterification of carboxylic acids with alcohols and phenols.

### 2. Experimental

#### 2.1. Preparation of *N*-(diphenylphosphino) triethylammonium chloride (**1**)

To a two-necked flask containing triethylamine (15.0 mmol, 2.0 mL), chlorodiphenylphosphine (10.0 mmol, 1.8 mL) was added drop wise with vigorous stirring. Stirring was continued for 5 min at 50°C to obtain the product as a white solid. The produced *N*-(diphenylphosphino) triethylammonium chloride (**1**) was washed with diethyl ether (3×5 mL) to remove the remaining substrates, then filtered and dried under vacuum. (3.0 g, 93%), m.p.: 120-122 °C; IR (KBr): 3055 (=CH), 2974 (C-H), 2937 (C-H), 1590 (C=C), 1475 (C=C), 1178 (C-N), 1128 (P-Ph), 961 (P-N) cm<sup>-1</sup>; δ<sub>H</sub> (250 MHz, CDCl<sub>3</sub>) 7.30-6.87 (10H, m, Ph), 2.64 (6H, m, CH<sub>2</sub>), 0.88 (9H, t, *J* 7.5 Hz, Me); δ<sub>C</sub> (62.9 MHz, CDCl<sub>3</sub>) 131.78, 131.74, 131.15, 130.99, 130.64, 130.46, 128.38, 128.16, 45.88, 8.63.

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## 2.2. Preparation of *N*-diphenylphosphino triethylammonium *p*-toluenesulfonate (IL-6)

To a stirred solution of 1 (5.0 mmol, 1.6 g) in dichloromethane (5.0 mL), *p*-toluenesulfonic acid (5.0 mmol, 0.95 g) was added at reflux conditions. The reaction mixture was left to stir 48 h. Then, the solvent was evaporated and the product was washed with diethyl ether (2×5 mL), separated and dried under vacuum. *N*-(diphenylphosphino)triethylammonium *p*-toluenesulfonate (IL-6) was obtained as a pale-yellow liquid in 87% yield (2.0 g).

## 2.3. Typical procedure for the conversion of benzoic acid to benzyl benzoate (Shintou et al., 2003)

Benzoic acid (1.2 mmol, 0.146 g) was added to a stirred mixture of *N*-bromosuccinimide (1.0 mmol, 0.177 g) in IL-6 (2.0 mL) at 80°C. Benzyl alcohol (1.0 mmol, 0.1 mL) was then added to the reaction mixture. TLC monitoring showed the completion of the reaction after 4 h. Then the residue was dissolved in *n*-hexane (5 mL) and washed with saturated aqueous sodium carbonate (5 mL) to remove the excess of carboxylic acid. The organic layer was separated and the solvent was evaporated to give the pure benzyl benzoate (0.17 g, 80%) as a colourless oil;  $\delta_{\text{H}}$  (250 MHz, CDCl<sub>3</sub>) 7.98 (2H, dd, *J* 8.4, 1.5 Hz, Ph), 7.44-7.24 (8H, m, Ph), 5.26 (2H, s, CH<sub>2</sub>);  $\delta_{\text{C}}$  (62.9 MHz, CDCl<sub>3</sub>) 166.4, 136.1, 133.1, 130.2, 129.7, 128.6, 128.4, 128.3, 128.2, 66.7.

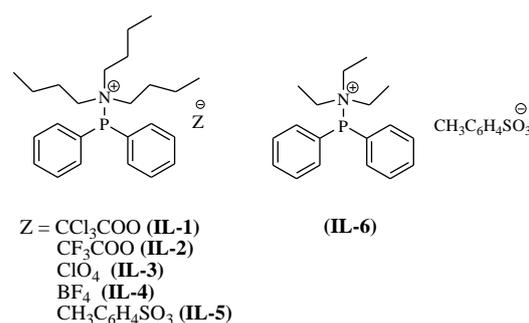
## 2.4. Typical procedure for the conversion of benzoic acid to phenyl benzoate (Iranpoor et al., 2008)

A mixture of *N*-bromosuccinimide (1.0 mmol, 0.177 g), benzoic acid (1.2 mmol, 0.146 g) in IL-6 (2.0 mL) was stirred at 80°C. Then 1.0 mmole of phenol (0.094 g) was added to the resulting mixture. After completion of the reaction as monitored by TLC (4 h), 5 mL *n*-hexane and 5 mL aqueous sodium carbonate was added. The organic layer was separated. The pure product was obtained as colourless crystals after evaporation of the solvent (0.178 g, 90%);  $\delta_{\text{H}}$  (250 MHz, CDCl<sub>3</sub>) 8.19-8.15 (2H, d, *J* 8.2 Hz, Ph), 7.78-7.06 (8H, m, Ph);  $\delta_{\text{C}}$  (62.9 MHz, CDCl<sub>3</sub>) 165.1, 151.2, 133.7, 129.9, 129.6, 129.3, 128.7, 125.8, 121.5.

## 3. Results and Discussion

In the course of our interest in esterification reactions (Nowrouzi et al., 2012; Nowrouzi and Alizadeh, 2013), we observed that *N*-(diphenylphosphino)tributylammonium

trichloroacetate (IL-1) converted benzoic acid to benzyl benzoate in the presence of benzyl alcohol and *N*-bromosuccinimide at 50°C. This observation motivated us to design analogues of this IL by changing the anion and the cation parts and study their capability for esterification reaction. In this regard, the synthesized salts IL-1 to IL-6 with tributyl- and triethylammonium cation and perchlorate, trichloroacetate, trifluoroacetate, tetrafluoroborate, and *p*-toluenesulfonate counterions were liquid at room temperature (Scheme 1).



Scheme 1. Structures of ionic liquids

We then examined the efficiency of these ILs in the condensation of benzoic acid with benzyl alcohol as a model reaction (Table 1).

Table 1. Condensation of benzyl alcohol and benzoic acid in different ILs at 50°C<sup>a</sup>

Entry	Ionic Liquid <sup>b</sup>	Time	Yield (%) <sup>c</sup>
1	IL-1	24	80
2	IL-2	24	60
3	IL-3	24	65
4	IL-4	24	65
5	IL-5	5	78
6	IL-6	5	80
7 <sup>d</sup>	IL-6	4	80

<sup>a</sup>Reaction conditions: NBS (1.0 mmol), benzoic acid (1.2 mmol), benzyl alcohol (1.0 mmol), IL (2.0 mL), 50 °C.

<sup>b</sup>IL-1 to IL-6 are room temperature ionic liquids.

<sup>c</sup> Isolated yield.

<sup>d</sup>At 80 °C.

As shown in Table 1, the nature of the anion influences the activity of ionic liquids in the esterification reaction. When the IL is based on a sulfonate anion, the most suitable conditions are obtained and the esterification reaction is complete after 5 h (Table 1, Entry 5). But, the replacement of sulfonate by trichloro- and trifluoroacetate, perchlorate or tetrafluoroborate greatly reduces the efficiency of the system. Changing the ammonium

part of the IL from tributylammonium to triethylammonium did not have a substantial effect on the progress of the reaction and two ILs are equally effective, although the structures of their ammonium parts are different.

On the basis of the results given in Table 1, and since the yield of the reaction for preparation of *N*-(diphenylphosphino) triethylammonium *p*-toluenesulfonate (IL-6) is much higher than *N*-(diphenylphosphino) tributylammonium *p*-toluenesulfonate (IL-5), IL-6, which was easily obtained from the reaction of triethylamine and chlorodiphenylphosphine was selected as the most suitable reagent and media for performing the esterification reactions.

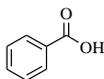
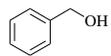
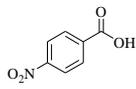
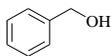
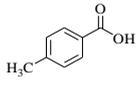
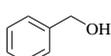
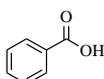
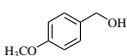
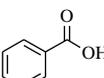
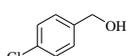
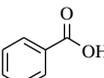
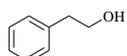
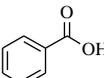
Apart from the ease of handling and preparation of this IL, the phosphine oxide formed in the reaction is taken up by the ionic liquid and the ester product forms a separate phase. On the other hand, immiscibility of ionic liquids with a number of organic solvents provides a solution for biphasic separation of the desired products. Therefore, here high conversions have been achieved with a convenience of separation of the ester product from the reaction mixture. This makes the workup much easier compared to triphenylphosphine (TPP). In the traditional Mitsunobu reaction using TPP (Mitsunobu et al., 1967 and 1971), one major problem that has somewhat hampered the reaction is the laborious purification of the product from phosphine oxide and costly and time-consuming chromatography is usually required to isolate the pure product, which results in reduced yield. Therefore, a great deal of effort has been directed towards modifying  $\text{Ph}_3\text{P}$  reagent to facilitate the isolation and purification of a desired product (Amos et al., 1983; Choi et al., 2003; Gentles et al., 2002; Iranpoor et al., 2005 and 2006; Lizarzaburu and Shuttleworth, 2003; McNulty et al., 2003; Silverman et al., 2001).

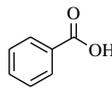
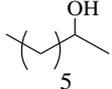
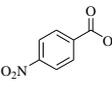
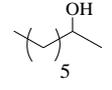
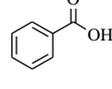
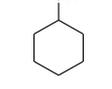
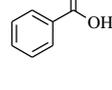
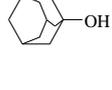
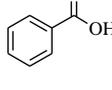
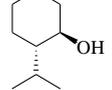
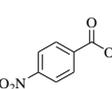
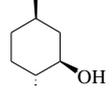
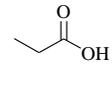
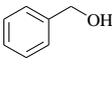
Optimization of the reaction conditions showed that, for a mixture of  $\text{NBS}/\text{RCO}_2\text{H}/\text{ROH}$ , a stoichiometric ratio of 1.0/1.2/1.0 mmol in IL (2.0 mL) was the most suitable. The effect of reaction temperature on this conversion was also investigated. The model reaction was repeated essentially under the optimal conditions except that the reaction was done at 80°C instead of 50°C. It can be clearly seen that increasing the temperature increases the rate of reaction (Table 1, Entries 6 and 7).

The optimized conditions were then applied to other acids and alcohols to produce the esterified products. The results of this investigation are given in Table 2. As shown, the esterified products were obtained in good to excellent yields for a wide array of carboxylic acids and alcohols. Benzylic, primary, and secondary alcohols reacted quantitatively,

yielding the esterified derivatives. Yields are high with both primary and secondary alcohols while no reaction occurred with tertiary alcohol 1-adamantanol (Table 2, Entry 11). The  $\beta$ -aryl alcohol 2-phenyl-1-ethanol reacted cleanly without styrene formation (Table 2, Entry 6), indicating that  $\beta$ -elimination does not occur. For electron-deficient benzyl alcohols, such as 4-chlorobenzyl alcohol, decreased yield of the product and longer reaction time was observed (Table 2, Entry 5). Electronic effects were investigated with the series of 4-substituted benzoic acids reacting with alcohols. Electron-deficient benzoic acids gave slightly better yields in shorter time while for electron-rich acids, such as 4-methylbenzoic acid, decreased yields of the products and longer reaction times were observed (Table 2, Entry 2 compared to Entry 3). Finally, propionic acid as an aliphatic acid appears to react without difficulty (Table 2, Entry 14).

**Table 2.** Esterification reactions promoted by *N*-(diphenylphosphino) triethylammonium *p*-toluenesulfonate (IL-6)<sup>a</sup>

Entry	Acid	Alcohol	Time (h)	Yield % <sup>b</sup>
1			4	80
2			3	88
3			4.5	76
4			3	75
5			5	70
6			7	80
7			7	75

8			9	72
9			7.5	83
10			7	88
11			-	-
12			10	68
13			9	75
14			3	85

<sup>a</sup>The stoichiometric ratio of the reactants for NBS/RCO<sub>2</sub>H/ROH in IL-6 (2.0 mL) is 1.0/1.2/1.0.

<sup>b</sup> Isolated yield.

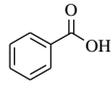
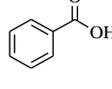
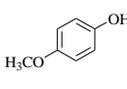
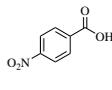
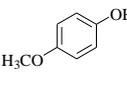
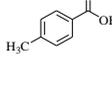
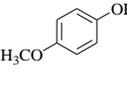
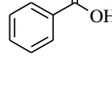
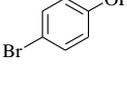
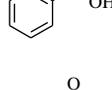
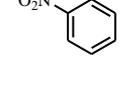
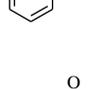
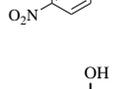
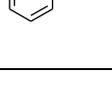
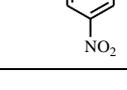
To find more applications for these ILs, we were especially interested in broadening the scope of our new IL for the preparation of phenolic esters. The condensation reaction between carboxylic acids and *ortho*- or *para*-substituted phenols were carried out in *N*-(diphenylphosphino) triethylammonium *p*-toluenesulfonate (IL-6) to afford the desired products. The optimized stoichiometric ratio of NBS/RCO<sub>2</sub>H/ArOH for the conversion of phenol to phenyl benzoate was found to be 1.0/1.2/1.0.

We thereafter used the optimized conditions for the synthesis of phenolic esters. Table 3 lists the successful results of the esterification between various carboxylic acids with different substituents on the phenolic component using IL-6. The reaction of benzoic acid with electron-rich phenol (Table 3, Entries 2-4) was successful and gave the desired esters in good to excellent yields. On the other hand, the presence of electron-withdrawing groups on the phenol ring decreases the overall yield of reaction (Table 3, Entries 5-8). In addition to the electronic factors, steric factors also affected the

reaction in terms of time and yield. Comparison of entries 6 and 7 indicate that existence of *ortho* substituent on the phenol ring, slightly decrease the yield and increase the time of the reaction.

The stereochemical implications of the reaction were then investigated utilizing chiral secondary alcohol *L*-menthol. The reaction of *L*-menthol with benzoic acid proceeded in the IL in the presence of *N*-bromosuccinimide at 80°C for 10 h to give the ester in 68 % isolated yield with a high degree of retention of stereochemistry (Table 2, Entries 12,13) (McNulty et al., 2003; Shintou et al., 2003; Silverman et al., 2001).

**Table 3.** Preparation of phenolic esters using *N*-(diphenylphosphino) triethylammonium *p*-toluenesulfonate (IL-6)<sup>a</sup>

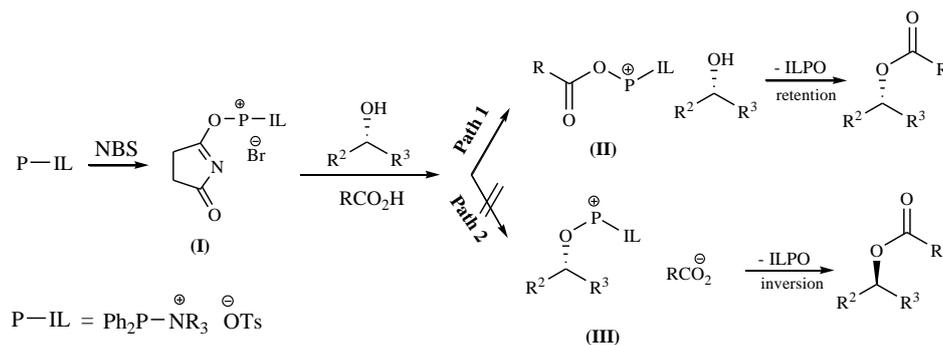
Entry	Acid	Phenol	Time (h)	Yield % <sup>b</sup>
1			4	90
2			3	87
3			2.5	95
4			3	85
5			4	90
6			10	75
7			8	80
8			24	50

<sup>a</sup>The molar ratio of the reactants for NBS/RCO<sub>2</sub>H/ArOH in IL-6 (2.0 mL) is 1.0/1.2/1.0

<sup>b</sup> Isolated yield

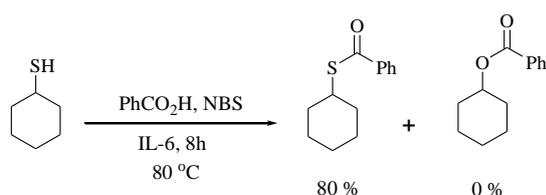
To explain the results obtained in our studies, the mechanism outlined in Scheme 2 is postulated. The

initial step involves nucleophilic addition of the phosphorous atom in the IL to the *N*-bromosuccinimide to give **(I)**. The subsequent step involves nucleophilic attack of the carboxylate anion on **(I)** to form an activated acyloxyphosphonium ion **(II)** (Scheme 2, Path 1). Finally,  $S_N2$ -type displacement by the alcohol on **(II)** with loss of phosphine oxide produces the ester with retention of stereochemistry. The competitive pathway leading to inversion of stereochemistry *via* the alkoxyphosphonium ion **(III)** is outlined in



**Scheme 2.** Possible mechanism for esterification reaction

In addition to stereochemistry, the reaction of a carboxylic acid and thiol could also confirm the proposed mechanism. In this way, cyclohexanethiol (1.0 mmol, 0.12 mL) was added to a mixture of NBS (1.0 mmol, 0.177 g), benzoic acid (1.2 mmol, 0.146 g) in IL-6 (2.0 mL) at 80°C. After 8 h, *S*-cyclohexyl benzothioate was obtained in 80% yield (Scheme 3). Formation of thioester, is consistent with the existence of intermediate **(II)** in the reaction mixture.



**Scheme 3.** Formation of thioester

#### 4. Conclusion

In Summary, a new class of phosphorous-based ionic liquids derived from simple amines have been introduced that can be applied to efficient condensation reactions of carboxylic acids with alcohols and phenols to provide esters under neutral conditions. The ease of preparation, cheapness and stability of these ILs gives them advantages over previously reported ILs used for this transformation. Other advantages of using this class

Scheme 2, Path 2. However, since esters with retention of stereochemistry are formed, the major reaction appears to follow Path 1, proceeding *via* the acyloxyphosphonium ion intermediate **(II)**. The substituent effect on the reaction conversion with 4-substituted benzoic acid (Table 2, Entries 2, 3, 9 and 13) indicate that 4-nitrobenzoic acid forms the acyloxyphosphonium salt with **(I)** faster, likely due to its greater acidity.

of ILs are convenience of the product separation from the reaction mixture because of the immiscibility of ester and also organic solvents with ILs. This is a definite advantage using ionic liquids over the homogeneous reaction conditions where the product is separated from the mixture by processes such as chromatography.

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#### References

- Amos, R. A., Emblidge, R. W., & Havens, N. (1983). Esterification using a polymer-supported phosphine reagent. *J. Org. Chem.*, 48, 3598–3600.
- Arfan, A., & Bazureau, J. P. (2005). Efficient combination of recyclable task specific ionic liquid and microwave dielectric heating for the synthesis of lipophilic esters. *Org. Proc. Res. & Dev.*, 9, 743–748.
- Choi, M. K. W., He, H. S., & Toy, P. H. (2003). Direct radical polymerization of 4-styryldiphenylphosphine: Preparation of cross-linked and non-cross-linked triphenylphosphine-containing polystyrene polymers. *J. Org. Chem.*, 68, 9831–9834.
- Cole, A. C., Jensen, J. L., Ntai, I., Tran, K. L. T., Weaver, K. J., Forbes, D. C., & Davis, J. H. (2002). Novel Brønsted acidic ionic liquids and their use as dual solvent-catalysts. *J. Am. Chem. Soc.*, 124, 5962–5963.
- Fraga-Dubreuil, J., Bourahla, K., Rahmouni, M., Bazureau, J. P., & Hamelin, J. (2002). Catalysed

- esterifications in room temperature ionic liquids with acidic counteranion as recyclable reaction media. *Catal. Commun.*, 3, 185–190.
- Franklin, A. S. (1998). Carboxylic acids and esters. *J. Chem. Soc., Perkin Trans. 1*, 2451–2466.
- Franklin, A. S. (1999). Carboxylic acids and esters. *J. Chem. Soc., Perkin Trans. 1*, 3537–3554.
- Gentles, R. G., Wodka, D., Park, D. C., & Vasudevan, A. (2002). Standardization protocols and optimized precursor sets for the efficient application of automated parallel synthesis to lead optimization: a Mitsunobu example. *J. Comb. Chem.*, 4, 442–456.
- Gui, J., Cong, X., Liu, D., Zhang, X., Hu, Z., & Sun, Z. (2004). Novel Brønsted acidic ionic liquid as efficient and reusable catalyst system for esterification. *Catal. Commun.*, 5, 473–477.
- Iranpoor, N., Firouzabadi, H., & Jamalian, A. (2005). Silphos [PCl<sub>3-n</sub>(SiO<sub>2</sub>)<sub>n</sub>]: a heterogeneous phosphine reagent for formylation and acetylation of alcohols and amines with ethyl formate and acetate. *Tetrahedron Lett.*, 46, 7963–7966.
- Iranpoor, N., Firouzabadi, H., Jamalian, A., & Kazemi, F. (2005). Silicaphosphine (Silphos): a filterable reagent for the conversion of alcohols and thiols to alkyl bromides and iodides. *Tetrahedron*, 61, 5699–5704.
- Iranpoor, N., Firouzabadi, H., & Jamalian, A. (2006). Silphos [PCl<sub>3-n</sub>(SiO<sub>2</sub>)<sub>n</sub>]: a heterogeneous phosphine reagent for the conversion of epoxides to β-bromoformates or alkenes. *Tetrahedron*, 62, 1823–1827.
- Iranpoor, N., Firouzabadi, H., Khalili, D., & Motevalli, S. (2008). Easily prepared azopyridines as potent and recyclable reagents for facile esterification reactions. an efficient modified Mitsunobu reaction. *J. Org. Chem.*, 73, 4882–4887.
- Izumi, J., Shiina, I., & Mukaiyama, T. (1995). An efficient esterification reaction between equimolar amounts of free carboxylic acids and alcohols by the combined use of octamethylcyclotetrasiloxane and a catalytic amount of titanium(IV) chloride tris(trifluoromethanesulfonate). *Chem. Lett.*, 24, 141–142.
- Larock, R. C. (1999). *Comprehensive Organic Transformations*. 2nd ed.; VCH: New York, NY.
- Lizarzaburu, M. E., & Shuttleworth, S. J. (2003). Convenient preparation of aryl ether derivatives using a sequence of functionalized polymers. *Tetrahedron Lett.*, 44, 4873–4876.
- McNulty, J., Capretta, A., Laritchev, V., Dyck, J., & Robertson, A. J. (2003). Dimethylmalonyltrialkylphosphoranes: new general reagents for esterification reactions allowing controlled inversion or retention of configuration on chiral alcohols. *J. Org. Chem.*, 68, 1597–1600.
- Mitsunobu, O., & Eguchi, M. (1971). Preparation of carboxylic esters and phosphoric esters by the activation of alcohols. *Bull. Chem. Soc. Jpn.*, 44, 3427–3430.
- Mitsunobu, O., Yamada, M., & Mukaiyama, T. (1967). Preparation of esters of phosphoric acid by the reaction of trivalent phosphorus compounds with diethyl azodicarboxylate in the presence of alcohols. *Bull. Chem. Soc. Jpn.*, 40, 935–939.
- Nowrouzi, N., & Alizadeh, S. Z. (2013). Benzoyl peroxide–imidazole: a novel and efficient reagent for the mild conversion of alcohols or phenols into benzoates. *Tetrahedron Lett.*, 54, 2412–2414.
- Nowrouzi, N., Mehranpour, A. M., & Ameri Rad, J. (2012). A simple and convenient method for preparation of carboxylic acid alkyl esters, phenolic and thioesters using chlorodiphenylphosphine/I<sub>2</sub> and imidazole reagent system. *Tetrahedron*, 66, 9596–9601.
- Okuhara, T., Kimura, M., Kawai, T., Xu, Z., & Nakato, T. (1998). Organic-reactions in excess water catalyzed by solid acids. *Catal. Today*, 45, 73–77.
- Otera, J., Dan-oh, N., & Nozaki, H. (1991). Novel template effects of distannoxane catalysts in highly efficient transesterification and esterification. *J. Org. Chem.*, 56, 5307–5311.
- Otera, J. (2003). *Esterification Methods, Reactions and Applications*. Wiley-VCH: Weinheim, Germany.
- Shintou, T., Kikuchi, W., & Mukaiyama, T. (2003). Efficient method for the preparation of carboxylic acid alkyl esters or alkyl phenyl ethers by a new-type of oxidation–reduction condensation using 2,6-dimethyl-1,4-benzoquinone and alkoxydiphenylphosphines. *Bull. Chem. Soc. Jpn.*, 76, 1645–1667.
- Silverman, R. B., Forrester, M. T., & Gomez-Vidal, J. A. (2001). Mild and selective sodium azide mediated cleavage of *p*-nitrobenzoic esters. *Org. Lett.*, 3, 2477–2479.
- Welton, T. (1999). Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.*, 99, 2071–2084.
- Wilkes, J. S. (2002). A short history of ionic liquids—from molten salts to neoteric solvents. *Green Chem.*, 4, 73–80.
- Xing, H., Wang, T., Zhou, Z. & Dai, Y. (2005). Novel Brønsted-acidic ionic liquids for esterifications. *Ind. Eng. Chem. Res.* 44, 4147–4150.