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In situ generated $Ph_3P(OAc)_2$ as a novel reagent for the efficient acetylation of alcohols and thiols at room temperature

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ABSTRACT

Ph_3P, Br_2, and ammonium acetate are used for the in situ generation of $Ph_3P(OAc)_2$, which was characterized by different NMR techniques. The $Ph_3P(OAc)_2$ generated was used as a novel and efficient reagent for the acetylation of alcohols and thiols in acetonitrile at room temperature under homogeneous conditions. This reaction was also performed under heterogeneous conditions using 1,3,2,4-diazadiphosphetidine as an easily prepared, stable, and heterogeneous P(III) compound.

Due to the abundance of esters in natural compounds, they are considered important functional groups in organic synthesis.[1] Esters are synthesized through the reaction of alcohols with carboxylic acids[2] or acylating/formylating agents, or by transesterification.[3] Conversion of alcohols into their acetates in the presence of acetic anhydride or acetyl chloride as acetylating agents has been studied in the presence of a variety of catalysts such as DMAP,[4] *tert*-Bu_3P,[5] F-DMAP,[6] $Al(OTf)_3$,[7] $TiCl_3(OTf)$,[8] polymer-supported gadolinium triflate,[9] $Mg(NTf_2)_2$,[10] $RuCl_3$,[11] $ZrOCl_2{\cdot}8H_2O$,[12] $Mg(ClO_4)_2$,[13] $H_5PV_2Mo_{10}O_{40}$,[14] $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$,[15] ZnO,[16] ATPB (acetonyltriphenylphosphonium bromide),[17] $BiFeO_3$,[18] and [TMBSA][HSO_4].[19]

The use of ethyl acetate for the acetylation of alcohols has been carried out with catalysts or reagents such as PPh_3/CBr_4,[20] $H_6[PMo_9V_3O_{40}]$,[21] dodeca-tungsto(molybdo)phosphoric acid,[22] $[PCl_{3-n}(SiO_2)_n]$,[23] $TiCl_3(OTf)$,[8] and N-heterocyclic carbene catalysts.[24]

The reaction of alkyl halides with metal salts of carboxylic acids to produce the corresponding esters has been found to be unsuccessful due to side reactions.[20] However, due to the presence of a wide variety of alcohols in comparison to alkyl halides, esterification of carboxylic salts with alcohols is a more attractive strategy. For this purpose, Mitsunobu conditions have been employed as an important method for the activation of alcohols using Ph_3P/DEAD, or DIAD/sodium[25] or zinc[26] carboxylate. In order to remove the problems encountered with the handling of DEAD, recently, we have reported the use of azopyridines as alternative reagents for esterification reactions.[27]

In the absence of any Mitsunobu reagent, there are very limited reports on the direct esterification of alcohols via carboxylic salts, with examples including ROH/$RCO_2K/Ph_3P/CCl_4$[28] and ROH/TsIm/RCO_2Na/Et_3N/TBAI.[29] The former method[28] uses a combination of excess Ph_3P (2.0 equiv with respect to the alcohol) and CCl_4 at 55–60 °C. Apart from the disadvantage of using CCl_4, this method suffers from a lack of stereoselectivity and the reaction of secondary alcohols occurs with both inversion and racemization.

The acylation of thiols, themselves an important functionality in many biologically active compounds,[30] has been performed with different acylating agents catalyzed by a variety of catalysts such as, $[Cp_2Ti(OSO_2C_8F_{17})_2]$,[31] $Cu(OTf)_2$,[32] $Cp_2Zr(OPf)_2$,[33] bromodimethylsulfonium bromide,[34] $InCl_3$,[35] and Ag(OTf).[36] However, as far as we are aware, the acylation of thiols in the presence of halogen sources and Ph_3P has not been reported so far.

In continuation of our work on the reactions of alcohols, thiols, and amines in the presence of Ph_3P/Br_2 and nucleophiles,[37] we decided to study the use of the $Ph_3P/Br_2/NH_4OAc$ mixed reagent system for the acetylation of alcohols.

We first used a combination of Ph_3P, Br_2, and NH_4OAc for the acetylation of 3-phenylpropanol as a model study. The optimized conditions were found to be $PPh_3/Br_2/NH_4OAc$/alcohol (1.25:1.25:2.87:1) in CH_3CN at room temperature. The reaction was complete within 0.3 h and the corresponding acetate was obtained in 90% yield along with the formation of Ph_3PO (Table 1, entry 1).

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Table 1
Optimization of the P(III) source for the acetylation of 3-phenylpropanol

Entry	P(III) source	Molar (equiv)	Time (h)	Conversion (%)	Yield (%)
1	Ph_3P	1.25	0.3	100	90
2	**P_1**	0.62	0.7	100	90
3	**P_2**	0.41	0.7	100	89
4	**P_3**	0.31	0.7	100	92

The structure of $Ph_3P(OAc)_2$ was determined by different spectroscopy techniques. The ^1H NMR spectrum of this reagent in CD_3CN showed a singlet at 1.85 ppm for the two methyls of the acetoxy groups. Its ^{13}C NMR spectrum showed two singlets for the methyl and carbonyl groups of the two acetoxy functionalities at 20.9 and 172.0 ppm, respectively.[38] The NMR data obtained showed that both acetoxy groups were in identical environments, which could be due to the possibility of rapid exchange processes at room temperature. The $^{31}P–\{^1H\}$ spectral signal of $Ph_3P(OAc)_2$ appeared as a singlet at 45.0 ppm.

In order to perform the reaction under heterogeneous conditions, which allows easy separation of the produced phosphine oxide, we decided to replace PPh_3 with phosphazane oligomers, which we previously used as ligands for C–C coupling reactions.[39] We employed 1,3,2,4-diazadiphosphetidine dimer $[(PhNH)PNPh]_2$ (**P_1**) and trimer $[(PhNH)PNPh]_3$ (**P_2**) along with dinuclear $[(PhNH)P_2(NPh)_2]_2NPh$ (**P_3**)[40] as sources of P(III) (Fig. 1) in conjunction with Br_2 and NH_4OAc under the optimized reaction conditions.

Although the three phosphazanes **P_1**–**P_3** have similar connectivities, they showed different solubilities in organic solvents. Compounds **P_1** and **P_2** are soluble, however, **P_3** was insoluble in solvents such as ethyl acetate, acetonitrile, diethyl ether, and CH_2Cl_2.

The amount of each phosphazane was determined on the basis of the number of phosphorus atoms they contained. Therefore, 0.62, 0.41, and 0.31 molar equivalents of **P_1**–**P_3** provided equal numbers of P(III) sites for the reaction with one equivalent of the alcohol. As the results in Table 1 show, all three reactions were complete within 0.7 h and the isolated yields were found to be nearly the same. However, the reactions of **P_1** and **P_2** are homogeneous but with **P_3**, the reaction occurs heterogeneously, which provides a simpler work-up. On the basis of the higher atom economy with **P_3** compared to the other phospazanes, the heterogeneous nature of its reaction, and also the higher yield for its preparation, this P(III) compound was selected as the most suitable.

With these results in hand, next we optimized the order of addition using Ph_3P and also **P_3** as the sources of P(III). The best result was obtained when ammonium acetate was dissolved in refluxing CH_3CN and then was added to a stirred solution of a mixture of PPh_3/Br_2 or **P_3**/Br_2 in CH_3CN at room temperature. We observed the formation of 3-phenylpropyl acetate after 0.3 and 0.7 h respectively, in 90% and 92% isolated yields (Table 2, entries 1 and 2). The reaction of **P_3** occurs heterogeneously with 0.31 equiv, however in the case of Ph_3P, 1.25 equiv of PPh_3 was required and the reaction was homogeneous. The reaction with **P_3** is superior to that using PPh_3 in terms of the isolation of its phosphine oxide and the stoichiometry of the reagent. The use of sodium or potassium acetates, which are insoluble in CH_3CN, even under reflux conditions did not produce any product. We were also interested to see if the reaction proceeded in the presence of other halogen sources. We used NBS, NCS, and I_2 instead of Br_2, and observed that the reaction time in the presence of Br_2 was much shorter and the yield was higher (Table 2, entries 3–8).

We next applied our optimized reaction conditions as a new approach for the acetylation of various primary and secondary alcohols in acetonitrile at room temperature[41] and the results are shown in Table 3.

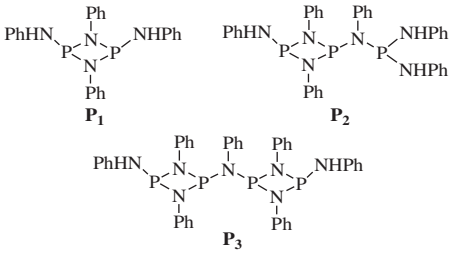


Figure 1. Structures of the phosphazanes.

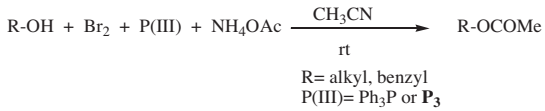
Table 2
Optimization of the halogen and acetate sources in the acetylation reaction with 3-phenylpropanol in acetonitrile at room temperature

Entry	Halogen source	P(III)	Acetate source	Time (h)	Yield (%)
1	Br_2	Ph_3P	NH_4OAc[a]	0.3	90
2	Br_2	**P_3**	NH_4OAc[a]	0.7	92
3	I_2	Ph_3P	NH_4OAc[a]	5	91
4	I_2	**P_3**	NH_4OAc[a]	7	92
5	NCS	Ph_3P	NH_4OAc[a]	7.5	90
6	NCS	**P_3**	NH_4OAc[a]	9	90
7	NBS	Ph_3P	NH_4OAc[a]	8	80
8	NBS	**P_3**	NH_4OAc[a]	10	78
9	Br_2	Ph_3P	NH_4OAc[b]	4	—[c]
10	Br_2	**P_3**	NH_4OAc[b]	4	—[c]
11	Br_2	Ph_3P or **P_3**	NaOAc[d]	4	—[c]
12	Br_2	Ph_3P or **P_3**	KOAc[d]	4	—[c]

[a] NH_4OAc was dissolved in CH_3CN on refluxing.
[b] NH_4OAc was added to the mixture without prior dissolution in hot CH_3CN.
[c] After 4 h, the reaction was incomplete and 3-phenylpropyl bromide was obtained in 50–60% yield.
[d] NaOAc and KOAc were added to the mixture without prior dissolution in hot CH_3CN.

The reaction of benzyl alcohol (Table 3, entry 8), under the optimized conditions, produced benzyl bromide as the major product. In order to decrease the formation of this bromination product, especially in the reaction of benzylic alcohols, we studied the use of NBS as the halogen source and found that on performing the reaction in an ice bath, acetylation of benzyl alcohol occurred predominantly and the amount of bromide by-product was reduced.

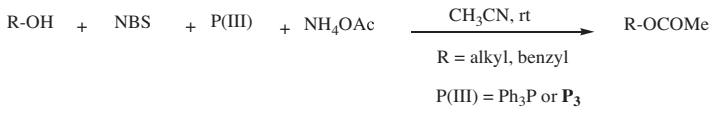
Table 3
Acetylation of alcohols in the presence of NH_4OAc



Entry	Alcohol	P(III)	Time (h)	Yield (%)[a]
1	$PhCH_2CH_2OH$	Ph_3P	0.3	91
		P_3	0.7	90
2	$PhCH_2CH_2CH_2OH$	Ph_3P	0.3	90
		P_3	0.7	92
3	$CH_3(CH_2)_{14}CH_2OH$	Ph_3P	0.3	95
		P_3	0.7	93
4	$CH_3(CH_2)_6CH_2OH$	Ph_3P	0.35	90
		P_3	0.75	88
5	$C_6H_{11}CH_2CH_2OH$	Ph_3P	0.33	90
		P_3	0.7	91
6	*l*-Menthol	Ph_3P	5	88 (8)
		P_3	7	84 (8)
7	$CH_3(CH_2)_5CH(OH)CH_3$	Ph_3P	4.5	87 (4)
		P_3	5.2	85 (5)
8	$PhCH_2OH$	Ph_3P	0.7	40 (53)
		P_3	2	34 (56)

[a] The yields in parenthesis refer to the corresponding bromides.

Table 4
Acetylation of benzylic alcohols in the presence of NH_4OAc



Entry	Alcohol	P(III)	Time (h)	Isolated yield[a] (%)
1	$PhCH_2OH$	Ph_3P	2	87 (3)
		P_3	1.5	70 (26)
2	*p*-$MeOC_6H_4CH_2OH$	Ph_3P	1.9	86 (6)
		P_3	1.5	72 (20)
3	*p*-$ClC_6H_4CH_2OH$	Ph_3P	9	84 (8)
		P_3	10	71 (24)
4	*p*-$NO_2C_6H_4CH_2OH$	Ph_3P	12	80 (10)
		P_3	12	69 (25)
5	*o*-$NO_2C_6H_4CH_2OH$	Ph_3P	15	78 (15)
		P_3	15	67 (28)
6	$PhCH(OH)CH_3$	Ph_3P	14	75 (14)
		P_3	14	70 (19)
7	Ph_2CHOH	Ph_3P	21	71 (17)
		P_3	21	69 (22)

[a] The yields in parenthesis refer to the corresponding bromides.

Table 5
Acylaton of thiols using Ph_3P or **P_3**.

Entry	Thiol	P(III)	Time (h)	Yield (%)
1	$PhCH_2SH$	Ph_3P	0.8	88
		Ph_3P[a]	6	85
		P_3	1	86
2	$CH_3(CH_2)_2CH_2SH$	Ph_3P	0.7	90
		P_3	0.8	91
3	$CH_3CH_2CH_2SH$	Ph_3P	0.65	87
		P_3	0.75	90
4	$CH_3(CH_2)_{10}CH_2SH$	Ph_3P	0.7	88
		P_3	0.75	92
5	$CH_3CH_2CH_2(SH)CH_3$	Ph_3P	3.5	80
		P_3	4.2	86
6	Cyclohexanethiol	Ph_3P	4.0	80
		P_3	5.0	85
7	$CH_3CH_2(CH_3)(SH)CH_3$	Ph_3P	8.0	75
		P_3	8.0	80

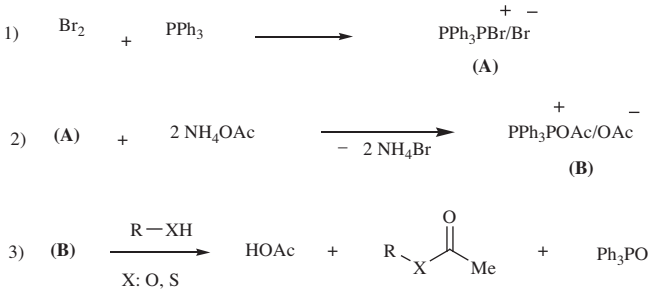
[a] NBS was used instead of Br_2 and an ice bath.

The optimized ratio of 2:1.9:2.3:1 (Ph_3P/NBS/NH_4OAc/alcohol) in CH_3CN in an ice bath was found to be the most suitable for the acetylation of benzylic alcohols homogeneously. In the case of using **P_3**, the optimized amount was found to be 0.5 molar equivalents with respect to the alcohol. We then applied these conditions for the acetylation of benzylic alcohols (Table 4).

Applying $Ph_3P(OAc)_2$ for the acetylation of *l*-menthol produced menthyl acetate in 88% isolated yield. Based on the comparison of the observed optical rotation of the obtained menthyl acetate {$[\alpha] = -70$, $c = 1$, $CHCl_3$} with the literature,[23] the reaction was found to occur with high retention of the configuration and optical purity (98% ee). Here again, comparison of the ^1H NMR spectrum of the obtained product with the literature,[42] confirmed that the reaction proceeded with retention of configuration.

After successful conversion of the various alcohols into their alkyl acetates, we also investigated the applicability of this reaction for the acetylation of thiols under the optimized conditions (Table 5).

According to the results in Table 5, thiols were also successfully converted into their corresponding thioacetates in high yields.[43] In comparison with the reaction of benzyl alcohol (Table 3, entry 8), the reaction of benzyl mercaptan with both Ph_3P or **P_3** and Br_2 or NBS did not produce any benzyl bromide as a side product (Table 5, entry 1).



Scheme 1. The proposed mechanism for the acetylation of alcohols and thiols using $Ph_3P/Br_2/NH_4OAc$.

According to the obtained results from the acetylation of *l*-menthol and the thiols, the following reaction mechanism which shows the retention of configuration is suggested (Scheme 1).

The isolation and characterization of Ph_3PO and NH_4Br can be regarded as additional evidence for the proposed mechanism.

In conclusion, we have introduced $Ph_3P(OAc)_2$ as a new and easily prepared reagent for the acetylation of alcohols and thiols at room temperature, homogeneously. The use of 1,3,2,4-diazadiphosphetidine (**P_3**), instead of Ph_3P, affords a similar reagent which can be used for the same transformations under heterogeneous conditions. Mechanistic studies showed that the reaction occurs with retention of configuration. In addition, the use of 1,3,2,4-diazadiphosphetidine (**P_3**) as an easily prepared, stable, and heterogeneous P(III) reagent in these transformations, shows the efficiency and advantages of this class of P(III) reagent in organic synthesis.

Acknowledgment

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References and notes

1. Ohshima, T.; Iwasaki, T.; Maegawa, Y.; Yoshiyama, A.; Mashima, K. *J. Am. Chem. Soc.* **2008**, *130*, 2944–2945.
2. (a) Sreedhar, B.; Arundhathi, R.; Amarnath Reddy, M.; Parthasarathy, G. *Appl. Clay Sci.* **2009**, *43*, 425–434; (b) Nowrouzi, N.; Mehranpour, A. M.; Ameri Rad, J. *Tetrahedron* **2010**, *66*, 9596–9601.

3. Grasa, G. A.; Singh, R.; Nolan, S. P. *Synthesis* **2004**, 971–985.
4. Steglich, W.; Hofle, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 981.
5. Vedejs, E.; Diver, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 3358–3359.
6. Legros, J.; Crousse, B.; Bonnet-Delpon, D. *J. Fluorine Chem.* **2008**, *129*, 974–977.
7. Kamal, A.; Khan, M. N. A.; Reddy, K. S.; Srikanth, Y. V. V.; Krishnaji, T. *Tetrahedron Lett.* **2007**, *48*, 3813–3818.
8. Firouzabadi, H.; Iranpoor, N.; Farahi, S. *J. Mol. Catal. A: Chem.* **2008**, *289*, 61–68.
9. Joon, H.-J.; Lee, S.-M.; Kim, J.-H.; Cho, H.-J.; Choi, J.-W.; Lee, S.-H.; Lee, Y.-S. *Tetrahedron Lett.* **2008**, *49*, 3165–3171.
10. Chakraborti, A. K.; Shivani *J. Org. Chem.* **2006**, *71*, 5785–5788.
11. De, S. K. *Tetrahedron Lett.* **2004**, *45*, 2919–2922.
12. Ghosh, R.; Maiti, S.; Chakraborty, A. *Tetrahedron Lett.* **2005**, *46*, 147–151.
13. Chakraborti, A. K.; Sharma, L.; Gulhane, R.; Shivani *Tetrahedron* **2003**, *59*, 7661–7668.
14. Farhadi, S.; Taherimehr, M. *Catal. Commun.* **2008**, *9*, 703–708.
15. Satam, J. R.; Jayaram, R. V. *Catal. Commun.* **2008**, *9*, 2365–2370.
16. Pericas, A.; Shafir, A.; Vallribera, A. *Tetrahedron* **2008**, *64*, 9258–9263.
17. Khan, A. T.; Choudhury, L. H.; Ghosh, S. *Eur. J. Org. Chem.* **2005**, *13*, 2782–2787.
18. Farhadi, S.; Zaidi, M. *J. Mol. Catal. A: Chem.* **2009**, *299*, 18–25.
19. Wang, W.; Cheng, W.; Shao, L.; Yang, J. *Catal. Lett.* **2008**, *121*, 77–80.
20. Hagiwara, H.; Morohashi, K.; Sakai, H.; Suzuki, T.; Ando, M. *Tetrahedron* **1998**, *54*, 5845–5852.
21. Heravi, M. M.; Bakhtiari, K.; Javadi, N. M.; Oskooie, H. A.; Bamoharram, F. F. *Monatsh. Chem.* **2007**, *138*, 445–447.
22. Tayebee, R.; Alizadeh, M. H. *Monatsh. Chem.* **2006**, *137*, 1063–1069.
23. Iranpoor, N.; Firouzabadi, H.; Jamalian, A. *Tetrahedron Lett.* **2005**, *46*, 7963–7966.
24. Grasa, G. A.; Guveli, T.; Singh, A.; Nolan, S. P. *J. Org. Chem.* **2003**, *68*, 2812–2819.
25. Varasi, M.; Walker, K. A. M.; Maddox, M. L. *J. Org. Chem.* **1987**, *52*, 4235–4238.
26. Rollin, P. *Synth. Commun.* **1986**, *16*, 611–616.
27. Iranpoor, N.; Firouzabadi, H.; Khalili, D.; Motevalli, S. *J. Org. Chem.* **2008**, *73*, 4882–4887.
28. Ramaiah, M. *J. Org. Chem.* **1985**, *50*, 4991–4993.
29. Soltani Rad, M. N.; Behrouz, S.; Faghihi, M. A.; Khalafi-Nezhad, A. *Tetrahedron Lett.* **2008**, *49*, 1115–1120.
30. Zheng, T. C.; Burkart, M.; Richardson, D. E. *Tetrahedron Lett.* **1999**, *40*, 603–606.
31. Qui, R.; Zhang, G.; Ren, X.; Xu, X.; Yang, R.; Luo, S.; Yin, S. *J. Org. Chem.* **2010**, *695*, 1182–1188.
32. Saravanan, P.; Singh, V. K. *Tetrahedron Lett.* **1999**, *40*, 2611–2614.
33. Qiu, R.; Zhu, Y.; Xu, X.; Li, Y.; Shao, L.; Ren, X.; Cai, X.; An, D.; Yin, S. *Catal. Commun.* **2009**, *10*, 1889–1892.
34. Khan, A. T.; Islam, S.; Majee, A.; Chattopadhyay, T.; Ghosh, S. *J. Mol. Catal. A: Chem.* **2005**, *239*, 158–165.
35. Chakraborti, A. K.; Gulhane, R. *Tetrahedron Lett.* **2003**, *44*, 6749–6753.
36. Das, R.; Chakraborty, D. *Synthesis* **2011**, 1621–1625.
37. (a) Iranpoor, N.; Firouzabadi, H.; Shaterian, H. R. *Synlett* **2000**, 65–66; (b) Iranpoor, N.; Firouzabadi, H.; Shaterian, H. R. *Tetrahedron Lett.* **2002**, *43*, 3439–3441; (c) Iranpoor, N.; Firouzabadi, H.; Nowrouzi, N. *Tetrahedron Lett.* **2008**, *49*, 4242–4244; (d) Iranpoor, N.; Firouzabadi, H.; Nowrouzi, N.; Firouzabadi, D. *Tetrahedron Lett.* **2006**, *47*, 6879–6881.
38. *Preparation and characterization of $Ph_3P(OAc)_2$:*
NH_4OAc (2.87 mmol, 0.221 g) was dissolved in refluxing CH_3CN (1.5 mL). This solution was then added to a flask containing a stirred mixture of Br_2 (1.25 mmol, 0.0625 mL) and Ph_3P (1.25 mmol, 0.327 g) in CH_3CN (1.5 mL) at room temperature. After stirring for 2.5 h at room temperature, the NH_4Br precipitate was removed by filtration. For spectroscopic studies, $Ph_3P(OAc)_2$ was prepared in CD_3CN. ^1H NMR (CD_3CN, 250 MHz): δ 1.85 (s, 6H), 7.4–7.58 (m, 15H). ^{13}C NMR (CD_3CN, 62.5 MHz): δ 20.9, 128.6, 131.4, 132.0, 132.8, 172.0 ppm.
^{31}P NMR (CD_3CN, 162 MHz): 45.0 ppm.
39. (a) Iranpoor, N.; Firouzabadi, H.; Tarrasoli, A.; Fereidoonnezhad, M. *Tetrahedron* **2010**, *66*, 2415–2421; (b) Iranpoor, N.; Firouzabadi, H.; Tarassoli, A.; Fereidoonnezhad, M. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 1367–1373.
40. Thompson, M. L.; Tarrasoli, A.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1987**, *26*, 684–689.
41. *Typical procedure for the conversion of 3-phenylpropanol into 3-phenylpropyl acetate using $Ph_3P/Br_2/NH_4OAc$:*
To a solution of $Ph_3P(OAc)_2$, was added 3-phenylpropanol (1 mmol, 0.137 mL). The progress of the reaction was monitored by TLC (Table 3, entry 2). After completion of the reaction (0.3 h) the reaction mixture was filtered to remove the precipitated NH_4Br followed by evaporation of the solvent. Column chromatography of the crude mixture on silica gel using *n*-hexane/EtOAc (3:1) as the eluent gave 3-phenylpropyl acetate in 90% yield (0.159 g). ^1H NMR ($CDCl_3$, 250 MHz): δ 1.88 (q, 2H, J = 7.5 Hz), 1.97 (s, 3H), 2.6 (t, 2H, J = 7.6 Hz), 4.0 (t, 2H, J = 6.5 Hz), 7.0–7.2 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 20.9, 30.1, 32.1, 63.8, 126.0, 128.3, 128.4, 141.1, 171.1 ppm.
42. McNaulty, J.; Capretta, A.; Laritchev, V.; Dyck, J.; Robertson, Al J. *J. Org. Chem.* **2003**, *68*, 1597–1600.
43. *Typical procedure for the conversion of benzyl mercaptan into benzyl thioacetate using $Ph_3P/Br_2/NH_4OAc$:*
The same mixture of Ph_3P, Br_2, and NH_4OAc was prepared as described above. Addition of benzyl mercaptan (1.0 mmol, 0.11 mL) and monitoring the reaction by TLC showed completion of the reaction after 0.8 h (Table 5, entry 1). Removal of the produced NH_4Br by filtration was followed by evaporation of the solvent. Column chromatography of the crude mixture on silica gel using *n*-hexane as the eluent, gave benzyl thioacetate in 88% yield (0.146 g). ^1H NMR ($CDCl_3$, 250 MHz): δ 2.3 (s, 3H), 4.1 (s, 2H), 7.26 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 30.3, 32.1, 127.2, 128.4, 128.6, 137.5, 193.1 ppm.