# 5,5′-Dimethyl-3,3′-azoisoxazole as a new heterogeneous azo reagent for esterification of phenols and selective esterification of benzylic alcohols under Mitsunobu conditions†

**Nasser Iranpoor,* Habib Firouzabadi* and Dariush Khalili**

*Received 17th March 2010, Accepted 17th June 2010*
**DOI: 10.1039/c004357e**



5,5′-Dimethyl-3,3′-azoisoxazole is used as a new efficient heterogeneous azo reagent for the highly selective esterification of primary and secondary benzylic alcohols and phenols with aliphatic and aromatic carboxylic acids *via* Mitsunobu protocols. The reaction is highly selective for primary benzylic alcohols *versus* secondary ones, aliphatic alcohols and also phenols. The isoxazole hydrazine byproduct can be simply isolated by filtration and recycled to its azoisoxazole by oxidation.

## Introduction

There are a number of chemical transformations that are highly profitable from a synthetic point of view, but often suffer from difficult purification steps. Infamous in this respect is the Mitsunobu reaction. In the Mitsunobu reaction, using the combination of a phosphine and azodicarboxylates activates alcohols (ROH) for attack by a range of relatively acidic pronucleophiles (NuH) to form the dehydrated coupled products (Nu–R).[1] Truly, the Mitsunobu reaction is a versatile method for the *in situ* conversion of aliphatic alcohols into alkylating agents under mild conditions. Although the Mitsunobu reaction was originally used for esterification,[2] a wide range of compounds that include amines,[3] azides,[4] ethers,[5] cyanides,[6] thiocyanides,[7] thioesters,[8] and thioethers[9] can be synthesized using similar protocols. This reaction historically faced purification challenges and often haunts the chemist in the isolation of the desired product. The separation of the reagent-derived byproducts, here, phosphine oxide and hydrazinodicarboxylate, from the desired condensation product is almost invariably the most time and resource consuming part of the Mitsunobu reaction. Due to the wide scope of the Mitsunobu reaction, a set of strategies were elaborated which provide quicker work-up procedures instead of using the tedious and time demanding classical chromatographic methods for the separation of products and spent reagents, and introduce alternatives to DEAD and triphenylphosphine (TPP). These efforts were latterly reviewed.[10] For example, Sugimura and co-workers recently published the details of the preparation and handling of di-2-methoxyethyl azodicarboxylate (DMEAD) in esterification reactions. The hydrazine of DMEAD can be mostly removed by a simple extraction with neutral water.[11] The ferrocenyl-tagged triphenylphosphine reagent has been used together with di-*tert*-butylazodicarboxylate in Mitsunobu reactions that do not require chromatographic purification of the desired product.[12] Besides, polymer-supported reagents,[13] fluorous azo and phosphine reagents whose by-products could be separated either by fluorous flash chromatography or fluorous solid-phase separation,[14] using acidic or basic workup of reaction mixture[15] and ring opening metathesis (ROM)[16] are other assortments that provide solutions for the separation problem in the Mitsunobu reaction. However, the precious nature of many of these reagents, in connection with the scarcity of their commercial availability, addition of time and limitation of scope probably precludes their use in usual organic synthesis. The mentioned laborious purification encountered with this reaction and motivation for extension of this important reaction in our research group,[17] prompted us to design new heterogeneous azo reagents that suggest an attractive approach to solve the separation problem in the Mitsunobu reaction. After an extensive survey of the literature, we were unable to gain any examples detailing the use of heterogeneous azo reagents in the Mitsunobu reaction. This work is the first successful attempt to apply these reagents that are heterogeneous in essence in the Mitsunobu reaction. So, we herein report our observation on the synthesis and use of the new azo compound 5,5′-dimethyl-3,3′-azoisoxazole, for the preparation of a series of benzylic and phenolic esters in Mitsunobu reaction.

## Results and discussion

We have recently reported the first use of azo pyridines for the Mitsunobu reaction.[18] Among them, the use of 4,4′-azopyridine offers rapid purification by simple filtration of the produced insoluble hydrazine. Furthermore, we have already found that *N*-alkyl salts of azopyridines have lower reactivity compared to that of azo pyridines in esterification processes. This study points to the great electronic effect of the pyridinium rings on the basicity of the obtained adduct from the reaction of $PPh_3$ and the azo reagent. Based on this observation, we aimed to investigate whether aryl azo compounds including two heteroatoms such as N, O or S might behave similarly to *N*-alkyl pyridinium salts or not. Among the reported methods for the preparation of azo compounds[19] from deactivated aromatic amines, the cheap and readily available

*Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran. E-mail: iranpoor@susc.ac.ir, firouzabadi@susc.ac.ir; Fax: (+)98 711 2280926; Tel: +(98)7112284822*

† Electronic supplementary information (ESI) available: Detailed experimental procedure, more examples, characterization data for azo reagent **2d** and all ester products, and copies of $^1H$ or $^{13}C$ NMR spectra. See DOI: 10.1039/c004357e

**Table 1** Synthesis of symmetrical azo compounds **2a–d**

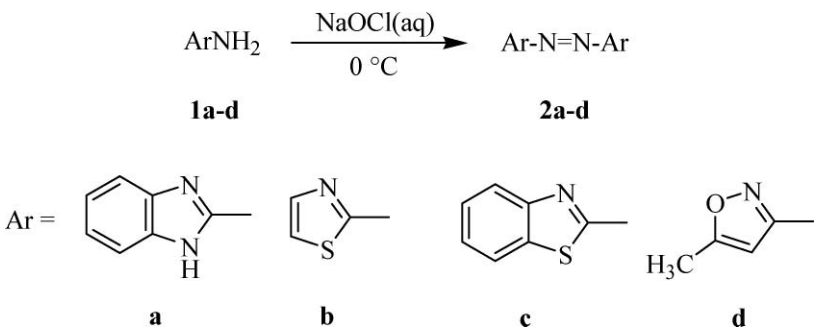
| Entry | $ArNH_2$ | ArN=NAr | Time/h | Yield (%) |
|---|---|---|---|---|
| 1 | **1a** | **2a** | 1 | 15 |
| 2 | **1b** | **2b** | 1 | 20 |
| 3 | **1c** | **2c** | 1 | 35 |
| 4 | **1d** | **2d** | 1 | 60 |

sodium hypochlorite (bleach),[20] has been found to be the most suitable one. Our initial investigation centered on the synthesis of a series of new symmetrical heteroaromatic azo compounds. The symmetrical azo compounds **2a–d** (see Scheme 1 for structures) were synthesized by the coupling of their readily available aromatic amines **1a–d** using 6–14% aqueous solution of NaOCl. We started with the coupling of 2-aminobenzimidazole **1a** to produce 2,2′-azobenzimidazole **2a**, but the isolated yield for the synthesis of **2a** was quite low (15%, Table 1).

Oxidation of 2-aminothiazole **1b** as a starting amine yielded 2,2′-azothiazole **2b** in low yield (20%, Table 1). Similarly, treatment of 2-aminobenzothiazole **1c** and 3-amino-5-methyl-isoxazole **1d** with sodium hypochlorite at 0 °C afforded 2,2′-azobenzothiazole **2c** and 5,5′-dimethyl-3,3′-azoisoxazole **2d** in 35% and 60% yield, respectively. We then studied the applicability of these azo compounds (**2a–d**) for esterification of benzyl alcohol with benzoic acid as a model reaction. The results of esterification obtained with these azo reagents in the presence of triphenylphosphine in refluxing acetonitrile are shown in Table 2.

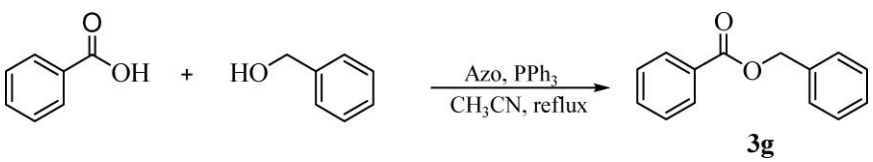
When 5,5′-dimethyl-3,3′-azoisoxazole **2d** was used, a clear difference in efficiency was observed. Indeed the use of azo **2d** provided the benzyl benzoate **3g** in 89% yield. In contrast, 2,2′-azobenzothiazole **2b** and **2c** gave the desired ester in 13 and 15% yields. In the case of using **2a**, no reaction took place (Table 2, entry 1). This difference in reactivity could be due to the presence of more electronegative atoms (N and O) in **2d** which makes its azo group more prone to electrophilic addition of $PPh_3$. Therefore, 5,5′-dimethyl-3,3′-azoisoxazole was selected as the reagent of choice for transformation of acids/alcohols to their corresponding esters under Mitsunobu reaction conditions offering improved reactivity and yields. Initially, we used different organic solvents such as $CH_2Cl_2$, $CHCl_3$, $Et_2O$, THF and $CH_3CN$ to find the most suitable one. The best results were achieved using acetonitrile in terms of time and yield. Moreover, we found that in acetonitrile, 5,5′-dimethyl-3,3′-azoisoxazole **2d** is not soluble and its hydrazine can easily be removed from the reaction mixture by simple filtration. This hydrazine byproduct can be simply recycled to its azo compound **2d** by its oxidation with iodosobenzene diacetate in DMSO at 60 °C for 10 h.

Further optimization studies on the esterification of benzyl alcohol with benzoic acid revealed that using 1.1 equiv. of both **2d** and $PPh_3$, 1.3 equiv. of alcohol and 1.0 equiv. of acid gave a quantitative conversion of the acid/alcohol to benzyl benzoate. In an attempt to convert primary and secondary aliphatic alcohols such as 2-phenylethanol, 1-octanol and 2-octanol under Mitsunobu conditions to their esters, we observed that no reaction had taken place. Consequently, azo **2d** can be used as a selective reagent for esterification of only benzylic alcohols in Mitsunobu processes. We also probed the effect of sequential addition of azo, $PPh_3$ and acid in our study. Treating the preformed azo **2d**/$PPh_3$ adduct sequentially with a solution of acid followed by addition of alcohol gave nearly identical results to the addition of $PPh_3$ to the mixture of acid/azo **2d**, followed by addition of alcohol and no distinct

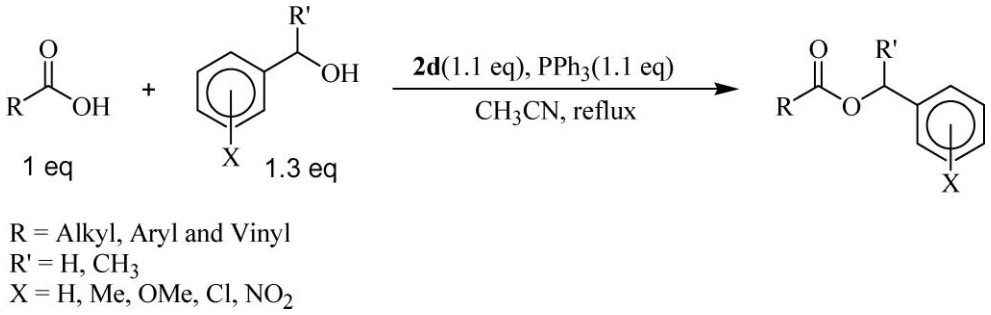



**Scheme 1**

**Table 2** Azo compounds **2a–d** for esterification of benzyl alcohol with benzoic acid under Mitsunobu conditions




| Entry | Azo | Time/h | Isolated yield of **3g** (%) |
|---|---|---|---|
| 1 | **2a** | 24 | 0 |
| 2 | **2b** | 24 | 13 |
| 3 | **2c** | 24 | 15 |
| 4 | **2d** | 6.5 | 89 |




**Scheme 2**



improvement in yield was observed. With the optimization studies completed, we examined a variety of primary and secondary benzylic alcohols with electron-donating and -withdrawing groups on the phenyl fragment and various aromatic and aliphatic acids (Scheme 2, Table 3).

Since esterification reactions of 4-nitrobenzoic acid are usually studied in Mitsunobu reactions,[21] we first applied our reaction conditions to this substrate. In its reactions, both electron-rich (–OMe and –Me) and electron-poor (–Cl and $–NO_2$) benzylic alcohols gave their corresponding esters in high yields. The applicability of the azo **2d** was also briefly probed by the reaction of the less acidic nucleophile, benzoic acid, with a series of benzyl alcohols that have different electronic and steric effects. There is little difference among donating groups such as –OMe and –Me in time and yield of esterification (Table 3, entries 8, 9 and 10). In addition, steric effects *via* introduction of an *ortho* group to the benzyl alcohol were examined. The results (entry 8 compared to 9) indicate that the yield of the ester formation dropped slightly as the bulk of the alcohol increases by *ortho* substituent. The stereospecificity of the reaction with 5,5′-dimethyl-3,3′-azoisoxazole **2d** was also studied using (*R*)-1-phenylethanol as a chiral secondary alcohol. By this method, the corresponding esters (*S*)-1-phenyl-1-ethyl benzoate **3m** was obtained in moderate yield (55%) with perfect inversion of stereochemistry. The configuration of the product was established by comparison of its optical rotation with the literature.[22] The reaction was also be carried out successfully when we used a less electron-deficient acid (lower $pK_a$) such as 4-methylbenzoic acid as a nucleophile. Further results, which illustrate the scope of this reagent, showed that aliphatic acids such as propanoic acid (Table 3, entries 18 and 19), crotonic acid (Table 3, entry 20) and undec-10-enoic acid (Table 3, entry 21) could be cleanly benzylated to afford the expected products **3r–3u**. Owing to the importance and application of fatty acid esters in industrials,[23] we applied successfully our reaction conditions for the esterification of stearic and oleic acids with benzyl alcohol (Table 3, entries 22 and 23).

Generally, the phenolic –OH group also participates as an acidic component in the Mitsunobu reaction, but it is surprising that very few reports have focused on the deliberate use of phenols as a nucleophile in the Mitsunobu reaction.[18,24] To gain insight into the efficiency of azo reagent **2d**, various phenols with electron-withdrawing and electron-donating groups were subjected to the Mitsunobu esterification in association with aliphatic and aromatic acids (Scheme 3).

The reaction proved to be quite efficient with various acids and phenols. The results are summarized in Table 4.

The conversion of phenol to phenyl benzoate was chosen to optimize the reaction conditions. Consistent with our previous optimization reactions, we selected refluxing acetonitrile as the solvent. Subjecting 1.2 equivalents of phenol to 1.0 equivalent of acid and 1.2 equivalents each of $PPh_3$ and 5,5′-dimethyl-3,3′-azoisoxazole **2d** resulted in 70% conversion to phenyl benzoate **4a** and incomplete consumption of azo **2d** and $PPh_3$. Decreasing the number of equivalents of azo **2d** and $PPh_3$ to 1.1 and increasing phenol to 1.3 equiv. led to the clean conversion of phenol to **4a**, isolated in 85% yield after purification. These reaction conditions were applied to a variety of substrates (Table 4).

After the successful esterification of the simple phenol (entry 1), we found that a variety of substitution patterns perform the reaction in good to high yields. Consequently, we found that the overall yield in this reaction depends mostly on the electronic nature of substituents on the phenol in such a manner that electron-donating groups increase the yield of esterification (Table 4, entries 2–4 compared to entries 5 and 6). The lowered reactivity of *ortho*-substituted alcohols is attributed to the increased steric hindrance around the –OH functional group. To investigate this further in the reaction of phenols with acids, a set of reactions using more encumbered phenols were performed. In this regard, 2,6-dimethylphenol, 2-isopropylphenol and 2-*tert*-butylphenol (Table 4, entries 7–9) were selected as more sterically demanding phenols in this study. Conversion of these phenols into their esters **4g–4i** was noticeably lower as determined by isolated yields after column chromatography. These results show that, similar to DEAD and DIAD, azo reagent **2d** is also sensitive to steric factors.[25]

As far as we know, none of the reported methods on Mitsunobu esterification using DEAD, and also our previous report using azopyridines,[18] have shown any selectivity between different classes of alcohols, so we hoped to observe some selectivity with our new heterogeneous azo compound **2d**. To investigate the selectivity of esterification of alcohols using 5,5′-dimethyl-3,3′-azoisoxazole **2d**, we set up some experiments using typical reaction conditions with equimolar amounts of different alcohols and observed excellent selectivity for esterification of benzylic alcohols *versus* aliphatic ones, primary benzylic alcohols *vs.* secondary ones and also benzylic alcohols *vs.* phenols. The results are summarized in Table 5.

**Table 3** Esterification of various benzylic alcohols under Mitsunobu reaction promoted by **2d**

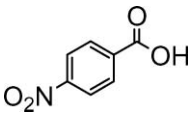
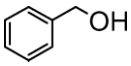
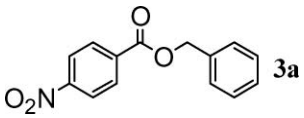
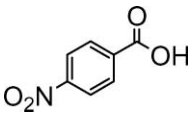
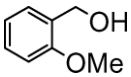
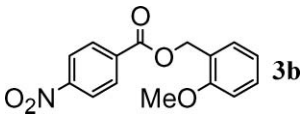
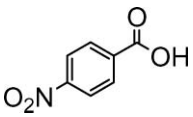
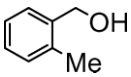
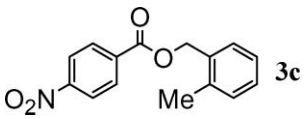
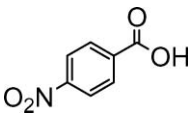
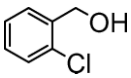
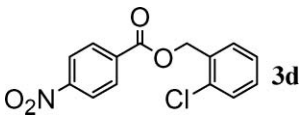
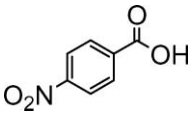
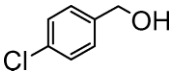
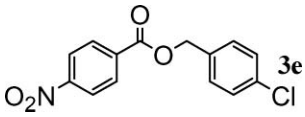
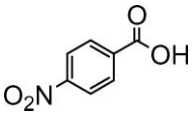
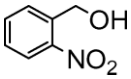
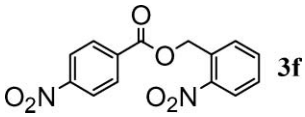
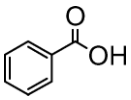
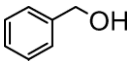
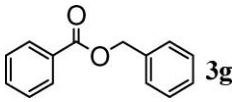
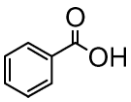
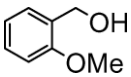
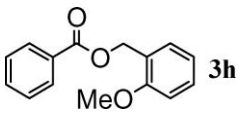
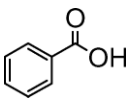
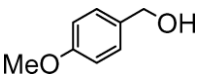
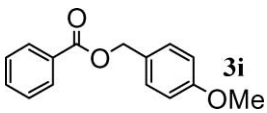
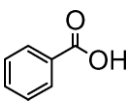
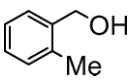
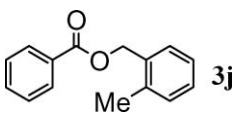
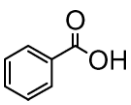
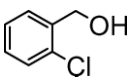
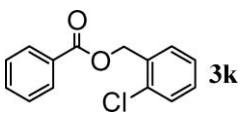
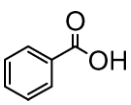
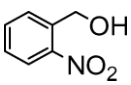
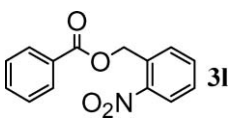
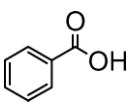
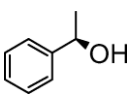
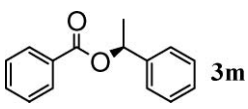
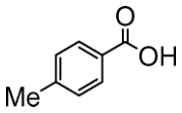
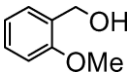
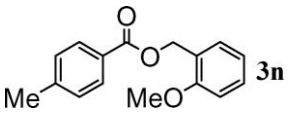
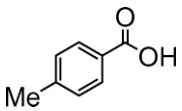
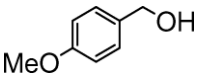
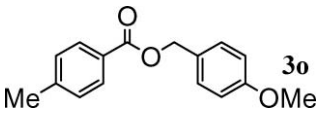
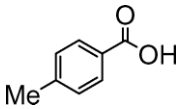
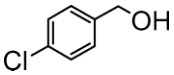
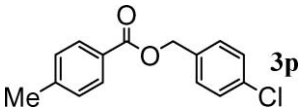
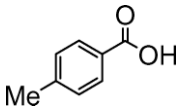
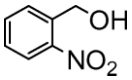
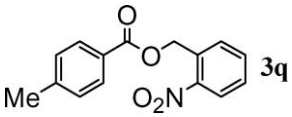
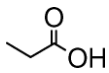
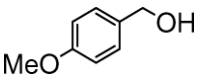
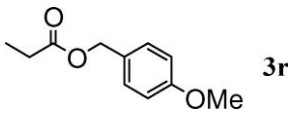
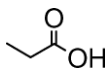
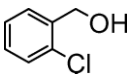
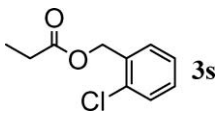
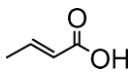
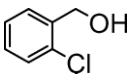
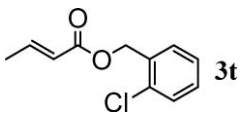
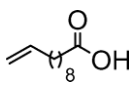
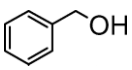
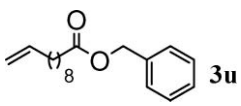
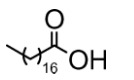
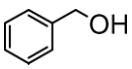
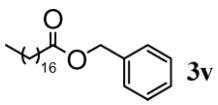
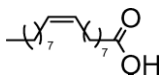
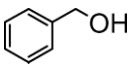
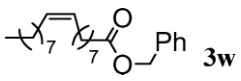
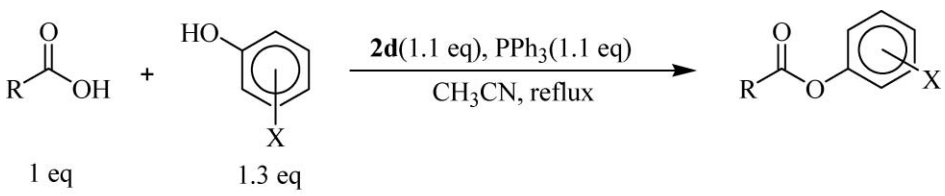
| Entry | $RCO_2H$ | ROH | Product | Time/h | Yield (%) |
|---|---|---|---|---|---|
| 1 |  |  |  **3a** | 5 | 89 |
| 2 |  |  |  **3b** | 4.5 | 89 |
| 3 |  |  |  **3c** | 5.5 | 86 |
| 4 |  |  |  **3d** | 6.5 | 83 |
| 5 |  |  |  **3e** | 6.5 | 85 |
| 6 |  |  |  **3f** | 8 | 80 |
| 7 |  |  |  **3g** | 6.5 | 89 |
| 8 |  |  |  **3h** | 6 | 87 |
| 9 |  |  |  **3i** | 5.5 | 90 |
| 10 |  |  |  **3j** | 6.5 | 85 |
| 11 |  |  |  **3k** | 8 | 83 |
| 12 |  |  |  **3l** | 9 | 77 |
| 13 |  |  |  **3m** | 11 | 55 |

**Table 3** *(Contd.)*

| Entry | $RCO_2H$ | ROH | Product | Time/h | Yield (%) |
|---|---|---|---|---|---|
| 14 |  |  |  **3n** | 7 | 82 |
| 15 |  |  |  **3o** | 6.5 | 86 |
| 16 |  |  |  **3p** | 8 | 82 |
| 17 |  |  |  **3q** | 9 | 73 |
| 18 |  |  |  **3r** | 7.5 | 85 |
| 19 |  |  |  **3s** | 9.5 | 80 |
| 20 |  |  |  **3t** | 9.5 | 73 |
| 21 |  |  |  **3u** | 9 | 70 |
| 22 |  |  |  **3v** | 9 | 70 |
| 23 |  |  |  **3w** | 8 | 71 |




R = Alkyl and aryl
X = -OMe, -Me, -Br, -Cl, -$^{i}$Pr, -$^{t}$Bu

**Scheme 3**

**Table 4** Synthesis of phenolic esters using 5,5′-dimethyl-3,3′-azoisoxazole **2d**

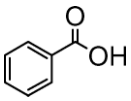
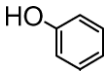
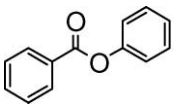
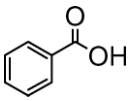
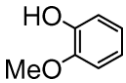
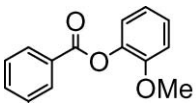
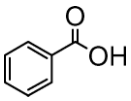
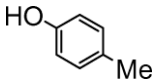
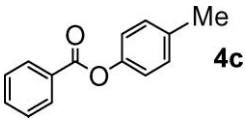
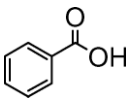
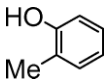
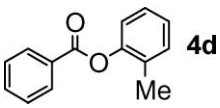
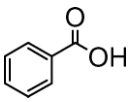
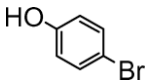
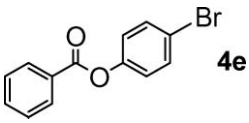
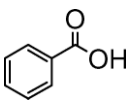
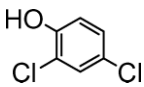
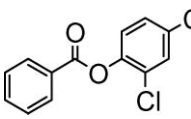
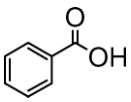
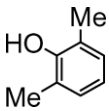
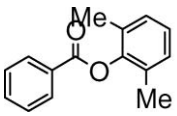
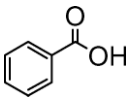
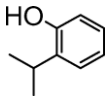
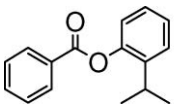
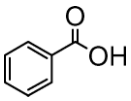
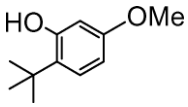
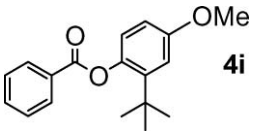
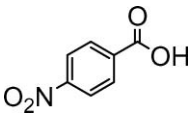
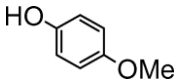
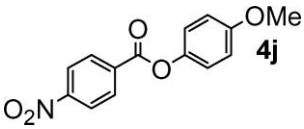
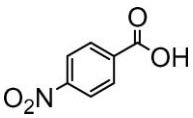
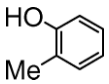
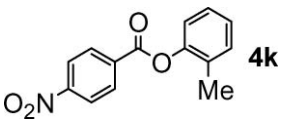
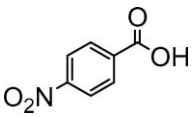
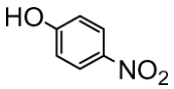
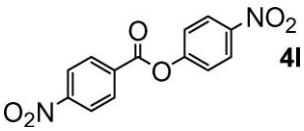
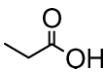
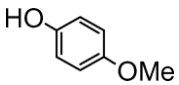
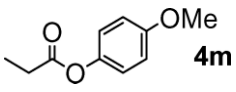
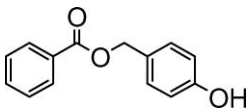
| Entry | Acid | Phenol | Product | Time/h | Yield (%) |
|---|---|---|---|---|---|
| 1 |  |  |  **4a** | 9.5 | 85 |
| 2 |  |  |  **4b** | 8.5 | 88 |
| 3 |  |  |  **4c** | 9 | 88 |
| 4 |  |  |  **4d** | 10 | 86 |
| 5 |  |  |  **4e** | 10.5 | 80 |
| 6 |  |  |  **4f** | 12 | 70 |
| 7 |  |  |  **4g** | 11.5 | 64 |
| 8 |  |  |  **4h** | 11 | 63 |
| 9 |  |  |  **4i** | 11.5 | 59 |
| 10 |  |  |  **4j** | 7.5 | 96 |
| 11 |  |  |  **4k** | 8.5 | 90 |
| 12 |  |  |  **4l** | 10.5 | 85 |
| 13 |  |  |  **4m** | 11 | 83 |

**Table 5** Selective conversion of various alcohols with benzoic acid in binary mixtures to corresponding esters using **2d** under Mitsunobu conditions[a]

| Entry | Binary mixture | Product: conversion (%)[b] | Time/h | Yield (%)[c] |
|---|---|---|---|---|
| 1 | Benzyl alcohol<br>1-Octanol | Benzyl benzoate: 100<br>1-Octyl benzoate: 0 | 7 | 85 |
| 2 | Benzyl alcohol<br>2-Octanol | Benzyl benzoate: 100<br>2-Octyl benzoate: 0 | 6.5 | 81 |
| 3 | Benzyl alcohol<br>1-Phenylethanol | Benzyl benzoate: 100<br>1-Phenylethyl benzoate: 4 | 7 | 84 |
| 4 | 1-Phenylethanol<br>1-Octanol | 1-Phenylethyl benzoate: 100<br>1-Octyl benzoate: 0 | 11 | 70 |
| 5 | 1-Phenylethanol<br>2-Octanol | 1-Phenylethyl benzoate: 100<br>2-Octyl benzoate: 0 | 11 | 69 |
| 6 | Benzyl alcohol<br>4-Methoxy phenol | Benzyl benzoate: 100<br>4-Methoxypheny benzoate: 0 | 6 | 89 |
| 7 | 4-Hydroxy benzyl alcohol |  | 5.5 | 85[d] |

[a] The molar ratio of $Ph_3P$/**2d**/binary mixture/acid is 1.1/1.1/1.3/1.0. [b] Analysis by $^1$H-NMR and GLC. [c] Isolated yield. [d] Only one product was isolated.

In Scheme 4, we offer a plausible mechanistic pathway and intermediates involved in the Mitsunobu reaction using azo 5,5′-dimethyl-3,3′-azoisoxazole **2d** based on the experimental data.

In addition to the observed optical rotation which supports the inversion of configuration, the isolation of triphenyl oxide and hydrazine by-products are considered as evidence for the proposed mechanism.

## Experimental

### General procedure for the synthesis of azo compounds

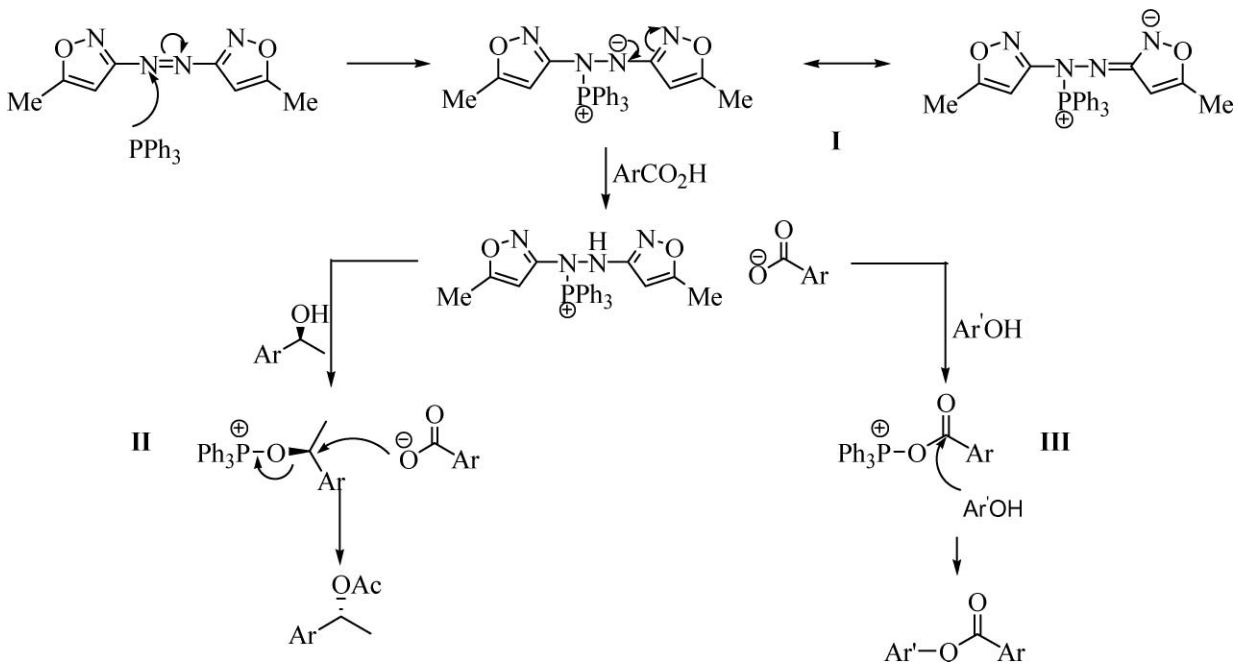
Azo compounds (**2a–d**) were prepared by oxidative coupling of their corresponding amines (**1a–d**) by sodium hypochlorite solution. A 50 mL aliquot of a cold solution of heterocyclic aromatic amine (25 mmol) in THF was added dropwise to mixture of 120 mL of sodium hypochlorite and 30 mL of water. The mixture was stirred at 0 °C as a colored precipitate formed. Filtration was performed a few minutes after the end of addition. The azo participates were collected and were used in our reactions without any purification.

### General procedure for the synthesis of benzylic esters using azo (2d)

To a flask containing a stirred mixture of acid (1 mmol) and azo compound (1.1 mmol) in refluxing acetonitrile (4 mL) was added $PPh_3$ (1.1 mmol). Benzylic alcohol (1.3 mmol) was then added to the reaction mixture. The reaction was monitored by TLC in *n*-hexane–ethyl acetate (9 : 1). After completion of the reaction, the solvent was evaporated and diethyl ether (15 mL) was added. The insoluble hydrazine was filtered off and the filtrate was evaporated to give a viscous oil. The purification was achieved using a short column of silica gel eluted with *n*-hexane–ethyl acetate (9 : 1).

### General procedure for the synthesis of phenolic esters using azo (2d)

Acid (1 mmol) and azo **2d** (1.1 mmol) were placed in a one-necked round bottom flask, acetonitrile (4 mL) was added to the mixture and heated at 80 °C. Triphenyl phosphine (1.1 mmol) and then phenol (1.3 mmol) were added to the reaction mixture. It was stirred for several hours. The progress of the reaction was monitored by TLC. After disappearance of the starting material, the solvent was evaporated. Diethyl ether (15 mL) was added and




**Scheme 4**

the solid hydrazine was filtered off. The residue was subjected to flash chromatography over silica gel by using *n*-hexane–ethyl acetate as eluent to give the corresponding ester.

## Conclusions

In this study, we have introduced a new heterogeneous azo reagent 5,5′-dimethyl-3,3′-azoisoxazole for the highly selective synthesis of benzylic and phenolic ester. The easy synthesis of this reagent in one step, facility in product isolation, separation of the hydrazine by-products and its recyclability are the most important advantages of this new azo reagent. In comparison with DEAD and azopyridines, we have demonstrated that combination of 5,5′-dimethyl-3,3′-azoisoxazole with $PPh_3$ is a highly selective system for the preparation of esters of primary benzylic alcohols in the presence of secondary ones and also phenols.

## Acknowledgements

We thank the Shiraz University Research Council for the financial support of this study.

## Notes and references

1 (*a*) O. Mitsunobu, *Synthesis*, 1981, 1; (*b*) D. L. Hughes, *Org. React.*, 1992, **42**, 335; (*c*) D. L. Hughes, *Org. Prep. Proced. Int.*, 1996, **28**, 127.
2 O. Mitsunobu and M. Yamada, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 2380.
3 (*a*) N. Morita and N. Krause, *Eur. J. Org. Chem.*, 2006, 4634; (*b*) A. H. Linares, D. Fourmy, J. L. Fourrey and A. Loukaci, *Synth. Commun.*, 2006, **36**, 487; (*c*) S. Buser and A. Vasella, *Helv. Chim. Acta*, 2005, **88**, 3151; (*d*) M. Lopez-Garcia, I. Alfonso and V. Gotor, *Chem.–Eur. J.*, 2004, **10**, 3006.
4 (*a*) P. H. Carter, G. D. Brown, S. R. Friedrich, R. J. Cherney, A. J. Tebben, Y. C. Lo, G. Yang, H. Jezak, K. A. Solomon, P. A. Scherle and C. P. Decicco, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 5455; (*b*) S. Chambert, A. Doutheau, Y. Queneau, S. J. Cowling, J. W. Goodby and G. J. Mackenzie, *J. Carbohydr. Chem.*, 2007, **26**, 27; (*c*) D. Gagnon, S. Lauzon, C. Godbout and C. Spino, *Org. Lett.*, 2005, **7**, 4769; (*d*) C. Xu and C. Yuan, *Eur. J. Org. Chem.*, 2004, 4410; (*e*) S. Goksu, C. Ozalp, H. Secén, Y. Sütbeyaz and E. Saripinar, *Synthesis*, 2004, 2849.
5 (*a*) P. Manivel, N. Premsai Rai, V. P. Jayashankara and P. N. Arunachalam, *Tetrahedron Lett.*, 2007, **48**, 2701; (*b*) D. Szabó, A. M. Bonto, I. Kövesdi, Á. Gömöry and J. Rábai, *J. Fluorine Chem.*, 2005, **126**, 639; (*c*) O. Renaudet and J. L. Reymond, *Org. Lett.*, 2004, **6**, 397; (*d*) S. L. Elmer and S. C. Zimmerman, *J. Org. Chem.*, 2004, **69**, 7363.
6 (*a*) A. Bussiere, V. Barragan-Montero, C. Clavel, L. Toupet and J. L. Montero, *Lett. Org. Chem.*, 2006, **3**, 654; (*b*) K. E. Elson, I. D. Jenkins and W. A. Loughlin, *Tetrahedron Lett.*, 2004, **45**, 2491; (*c*) T. Tsunoda, K. Uemoto, C. Nagino, M. Kawamura, H. Kaku and S. Itô, *Tetrahedron Lett.*, 1999, **40**, 7355.
7 (*a*) N. Iranpoor, H. Firouzabadi, R. Azadi and B. Akhlaghinia, *J. Sulfur Chem.*, 2005, **26**, 133; (*b*) H. Abe, S. Aoyagi and C. Kibayashi, *J. Am. Chem. Soc.*, 2005, **127**, 1473; (*c*) H. Abe, S. Aoyagi and C. Kibayashi, *J. Am. Chem. Soc.*, 2000, **122**, 4583.
8 (*a*) F. Wuest, K. E. Carlson and J. A. Katzenellenbogen, *Steroids*, 2008, **73**, 69; (*b*) K. Wojczykowski and P. Jutzi, *Synlett*, 2006, 39; (*c*) J. Müller, M. Brunnbauer, M. Schmidt, A. Zimmermann and A. Terfort, *Synthesis*, 2005, 998; (*d*) O. Schluze, J. Voss, G. Adiwidjaja and F. Olbrich, *Carbohydr. Res.*, 2004, **339**, 1787.
9 (*a*) J. S. W. Kwong, M. F. Mahon, M. D. Lloyd and M. D. Threadgill, *Tetrahedron*, 2007, **63**, 12601; (*b*) C. Schips and T. Ziegler, *J. Carbohydr. Chem.*, 2005, **24**, 773.
10 (*a*) K. C. Kumara Swamy, N. N. Bhuvan Kumar, E. Balaraman and K. V. P. Pavan Kumar, *Chem. Rev.*, 2009, **109**, 2551; (*b*) T. Y. Sze But and P. H. Toy, *Chem.–Asian J.*, 2007, **2**, 1340; (*c*) S. Dandapani and D. P. Curran, *Chem.–Eur. J.*, 2004, **10**, 3130; (*d*) R. Dembinski, *Eur. J. Org. Chem.*, 2004, 2763.
11 T. Sugimura and K. Hagiya, *Chem. Lett.*, 2007, **36**, 566.
12 (*a*) C. A. Fleckenstein and H. Plenio, *Adv. Synth. Catal.*, 2006, **348**, 1058; (*b*) For the tagged azo reagent see: S. Dandapani, J. J. Newsome and D. P. Curran, *Tetrahedron Lett.*, 2004, **45**, 6653.
13 (*a*) P. S. Humphries, Q.-Q. T. Do and D. M. Wilhite, *Beilstein J. Org. Chem.*, 2006, **2**, 21; (*b*) A. M. Harned, H. S. He, P. H. Toy, D. L. Flynn and P. R. Hanson, *J. Am. Chem. Soc.*, 2005, **127**, 52; (*c*) G. L. Thomas, C. Böhner, M. Ladlow and D. R. Spring, *Tetrahedron*, 2005, **61**, 12153; (*d*) G. L. Thomas, M. Ladlow and D. R. Spring, *Org. Biomol. Chem.*, 2004, **2**, 1679; (*e*) M. K. W. Choi, H. S. He and P. H. Toy, *J. Org. Chem.*, 2003, **68**, 9831; (*f*) J. H. Rigby and M. A. Kondratenko, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 1829; (*g*) P. H. Toy, T. S. Reger, P. Garibay, J. C. Garno, J. A. Malikayil, G.-Y. Liu and K. D. Janda, *J. Comb. Chem.*, 2001, **3**, 117.
14 (*a*) Q. Chu, C. Henry and D. P. Curran, *Org. Lett.*, 2008, **10**, 2453; (*b*) D. P. Curran, R. Bajpai and E. Sanger, *Adv. Synth. Catal.*, 2006, **348**, 1621; (*c*) D. P. Curran, X. Wang and Q. Zhang, *J. Org. Chem.*, 2005, **70**, 3716; (*d*) S. Dandapani and D. P. Curran, *J. Org. Chem.*, 2004, **69**, 8751; (*e*) A. P. Dobbs and C. McGregor-Johnson, *Tetrahedron Lett.*, 2002, **43**, 2807.
15 (*a*) M. Kiankarimi, R. Lowe, J. R. McCarthy and J. P. Whitten, *Tetrahedron Lett.*, 1999, **40**, 4497; (*b*) M. Von Itzstein and M. Mocerino, *Synth. Commun.*, 1990, **20**, 2049; (*c*) G. W. Starkey, J. J. Parlow and D. L. Flynn, *Bioorg. Med. Chem. Lett.*, 1998, **8**, 2385.
16 (*a*) D. Camp and I. D. Jenkina, *Aust. J. Chem.*, 1988, **41**, 1835; (*b*) G. Grynkiewicz, J. Jurcazk and A. Zamojski, *Tetrahedron*, 1975, **31**, 1411.
17 (*a*) N. Iranpoor, H. Firouzabadi, N. Nowrouzi and D. Khalili, *Tetrahedron*, 2009, **65**, 3893; (*b*) N. Iranpoor, H. Firouzabadi and N. Nowrouzi, *Tetrahedron*, 2006, **62**, 5498; (*c*) N. Iranpoor, H. Firouzabadi and N. Nowrouzi, *Tetrahedron Lett.*, 2006, **47**, 8247; (*d*) N. Iranpoor, H. Firouzabadi, B. Akhlaghinia and N. Nowrouzi, *Tetrahedron Lett.*, 2004, **45**, 3291; (*e*) N. Iranpoor, H. Firouzabadi, B. Akhlaghinia and R. Azadi, *Synthesis*, 2004, 92; (*f*) N. Iranpoor, H. Firouzabadi, G. H. Aghapour and A. R. Vaez Zadeh, *Tetrahedron*, 2002, **58**, 8689.
18 N. Iranpoor, H. Firouzabadi, D. Khalili and S. Motevalli, *J. Org. Chem.*, 2008, **73**, 4882.
19 (*a*) J. Park and J. Koh, *Dyes Pigm.*, 2009, **82**, 347; (*b*) E. Drug and M. Gozin, *J. Am. Chem. Soc.*, 2007, **129**, 13784; (*c*) I. Zadrozna and E. Kaczorowska, *Dyes Pigm.*, 2006, **71**, 207; (*d*) G. Cravotto, L. Boffa, M. Bia, W. Bonrath, M. Curini and G. A. Heropoulos, *Synlett*, 2006, 2605; (*e*) G. R. Srinivasa, K. Abiraji and C. Gowda, *Synth. Commun.*, 2003, **33**, 4221.
20 J. P. Launay, M. Tourrel-Paggis, J. F. Lipskier, V. Marvaud and C. Joachim, *Inorg. Chem.*, 1991, **30**, 1033.
21 (*a*) J. A. Dodge, J. I. Trujillo and M. Presnell, *J. Org. Chem.*, 1994, **59**, 234; (*b*) S. F. Martin and J. A. Dodge, *Tetrahedron Lett.*, 1991, **32**, 3017.
22 (*a*) T. Shintou, W. Kikuchi and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1645; (*b*) A. G. M. Barrett, D. C. Braddock, R. A. James, N. Koike and P. A. Procopiou, *J. Org. Chem.*, 1998, **63**, 6273; (*c*) K. Kabuto, M. Imuta, E. S. Kempner and H. Ziffer, *J. Org. Chem.*, 1978, **43**, 2357.
23 K. Mantri, K. Komura and Y. Sugi, *Synthesis*, 2005, 1939.
24 (*a*) V. P. Fitzjarrald and R. Pongdee, *Tetrahedron Lett.*, 2007, **48**, 3553; (*b*) N. Leclerc, M.-C. Pasareanu and A.-J. Attias, *Macromolecules*, 2005, **38**, 1531.
25 (*a*) X. Liao, Y. Wu and J. K. De Brabander, *Angew. Chem., Int. Ed.*, 2003, **42**, 1648; (*b*) A. B. Smith III, I. G. Safonov and R. M. Corbett, *J. Am. Chem. Soc.*, 2002, **124**, 11102; (*c*) I. Shin, M.-R. Lee, J. Lee, M. Jung, W. Lee and J. Yoon, *J. Org. Chem.*, 2000, **65**, 7667; (*d*) P. T. Gallagher, J. C. A. Hunt, A. P. Lightfoot and C. J. Moody, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2633.