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Communications

Efficient Method for Preparation of α-[(2,4-Dinitrobenzene)sulfonyl]oxy Carbonyl Compounds

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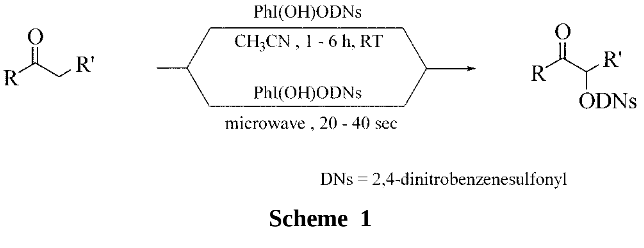
[Hydroxy(tosyloxy)iodo]benzene (Koser's reagent, HTIB) has been proved to be a versatile reagent in organic synthesis.[1] Among other applications, HTIB mediated α-tosyloxylation of carbonyl compounds has a particular significance with regard to the preparation of various useful compounds by nucleophilic substitution reactions.[2] It is well known that the α-organosufonyloxy carbonyl compounds allows the enhanced simplicity of reactivity patterns and faster reaction rates when compared to α-halo carbonyl compounds.[3,4] In general, α-halo carbonyl compounds have been used extensively as invaluable precursors in various organic transformations. However, the preparation of α-halo carbonyl compounds are not straightforward and its toxic and unstable nature made their uses in organic transformations practically undesirable.[5] Thus, the α-organosulfonyloxy carbonyl compounds have been emerged as substitutes for α-halo carbonyl compounds in nucleophilic organic transformations.[3] As interests in the use of HTIB in organic transformations become increasingly populated, the structural modifications of HTIB have been eagerly studied in order to alter its chemical reactivity. Accordingly, several analogous hypervalent iodine(III) compounds containing mesylate,[6] tosylate,[7] camphorsulfonate,[8] and nosylate[9] groups have been reported.

As part of our endeavor to the development of new hypervalent iodine(III) sulfonate reagents with high reactivity, we have found novel intermediary α-[(2,4-dinitrobenzene)sulfonyl]oxy aromatic ketones, generated *in situ* from reaction of aromatic ketones with [hydroxy(2,4-dinitrobenzenesulfonyloxy)iodo]benzene (HDNIB), readily converted to carboxylic acids in the presence of sodium periodate.[10] In addition, very recently we have also reported a new reaction that dealt with efficient conversion of α-[(2,4-dinitrobenzene)sulfonyl]oxy cycloakanones into dicarboxylic acid dimethyl esters using Oxone®.[11] On the other hand, the reaction of α-tosyloxy cycloalkanones at the same conditions afforded significantly reduced yields. The results of these studies clearly showed that the [(2,4-dinitrobenzene)sulfonyl]oxy (-ODNs) group has superior reactivity compared to that of -OTs group in nucleophilic substitution reactions. Therefore, it is expected that replacement of standard -OTs group with -ODNs group at alpha position to the carbonyl group should give faster reactions and high yields in the other nucleophilic organic transformations.

In this communications, we wish to describe an optimized preparation of the α-[(2,4-dinitrobenzene)sulfonyl]oxy carbonyl compounds at conventional reaction conditions along with preparation of the same compounds under solvent-free microwave irradiation conditions. The microwave (MW) accelerated organic reactions under solvent-free conditions have advantages over conventional reaction in solvents because of its environmentally friendly reaction conditions, faster reaction rates, high yields, and simple workup procedure.[12] Initially we have conducted α-sulfonyloxylation



Scheme 1

Table 1. Conversion of carbonyl compounds into α-[(2,4-dinitrobenzene)sulfonyl]oxy carbonyl compounds

Entry	R	R'	Yield (%)[a]	
			Conventional	M.W. Irradiation
1	Me	H	85	90
2	Et	Me	74	85
3	Ph	H	92	95
4	4-(Me)C_6H_4	H	89	93
5	4-(Cl)C_6H_4	H	87	90
6	Ph	Me	92	95
7	4-(Me)C_6H_4	Me	90	92
8	4-(Cl)C_6H_4	Me	88	88
9	-$(CH_2)_3$-		65	70
10	-$(CH_2)_4$-		70	75
11	Me	$COCH_3$	86	90
12	Ph	COOEt	82	90
13	EtO	COOEt	86	91

[a] Isolated yields.

at conventional reaction conditions. Thus, treatment of HDNIB with carbonyl compounds in acetonitrile provided α-[(2,4-dinitrobenzene)sulfonyl]oxy carbonyl compounds in high yields. The reactions were run at room temperature for less than 6 h and the results are summarized in the Table 1. The reactions were worked very well for the wide variety of carbonyl compounds which include aliphatic ketones, aromatic ketones, cyclic ketones, and β-dicarbonyl compounds. Among other solvents tested, acetonitrile was the solvent of choice in this method because of its ability to dissolve the salts. The required HDNIB can be easily prepared by the procedure reported from our recent report.[10] In general, hypervalent iodine(III) sulfonate reagents mediated α-oxysulfonylation reaction of carbonyl compounds required reflux temperatures in solvents (CH_3CN and CH_2Cl_2) and yields were usually moderate.[6-9] The room temperature reaction conditions achieved with HDNIB at present study might provide added flexibility for the utilities of α-sulfonyloxy carbonyl compounds for further applications in organic transformations. Given the success of introduction of [(2,4-dinitrobenzene)sulfonyl]oxy group to the alpha position of carbonyl compounds under conventional reaction conditions, we next examined the possibility of employing solvent-free microwave irradiation conditions to the same transformations. The reaction of the neat carbonyl compounds with HDNIB under microwave irradiation in household microwave oven readily provided the corresponding α-[(2,4-dinitrobenzene)sulfonyl]oxy carbonyl compounds in less than 40 sec. As shown in the Table 1, the microwave promoted method has been proved more efficient in terms of yields and reaction times compared to the conventional method in this study. We believe this successful results should promote the applications of hypervalent iodine(III) sulfonate reagents to the microwave induced organic reactions. Although microwave irradiation conditions proved to be superior to conventional conditions in this study, the use of room temperature reactions in solvent system may be advantageous for α-[(2,4-dinitrobenzene)sulfonyl]oxylation of carbonyl compounds in heat sensitive reaction conditions.

In conclusion, the α-[(2,4-dinitrobenzene)sulfonyl]oxylation of carbonyl compounds readily occurred for the broad range of carbonyl compounds utilizing both conventional and microwave irradiation promoted reaction conditions. General procedure under microwave irradiation is as follows. A ketone (1.0 mmol) and HDNIB (0.562 g, 1.2 mmol) were taken in a test tube and irradiated sequentially for 20-40 sec in 10 sec time intervals. The mixture was cooled down to room temperature, extracted with methylene chloride (2×20 mL), washed with H_2O and dried over $MgSO_4$. The solvent was evaporated and the residue was purified over silica gel using ethyl acetate-hexane (1 : 2) as eluent to give product. The conventional reactions could also carried out in acetonitrile at room temperature without use of microwave irradiation following above reaction procedures.

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References

1. (a) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365. (b) Koser, G. F. *Aldichimica Acta* **2001**, *34*, 89.
2. Prakash, O.; Saini, N.; Sharma, P. K. *Synlett* **1994**, 221.
3. Hoffman, R. V. *Tetrahedron* **1991**, *47*, 1109.
4. Hoffman, R. V.; Jankowski, B. C.; Carr, S. C. *J. Org. Chem.* **1986**, *51*, 130.
5. De Kimpe, N.; Verhé, R. *The Chemistry of α-Haloketones, α-Haloaldehydes and α-Haloimines*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1988.
6. (a) Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228. (b) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 210.
7. (a) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487. (b) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Epa, W. R.; Prakash, I. *J. Org. Chem.* **1989**, *54*, 1101.
8. Hatzigrigoriou, E.; Varvoglis, A.; Bakola-Christianopoulou, M. *J. Org. Chem.* **1990**, *55*, 315.
9. Lee, J. C.; Oh, Y. S.; Cho, S. H. *Bull. Korean Chem. Soc.* **1996**, *17*, 989.
10. Lee, J. C.; Choi, J.-H.; Lee, Y. C. *Synlett* **2001**, 1563.
11. Lee, J. C.; Ku, C. H. *Synlett* **2002**, 1679.
12. (a) Caddick, S. *Tetrahedron* **1995**, *51*, 10403. (b) Varma, R. S. *Green Chemistry* **1999**, 43. (c) Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* **2001**, *57*, 9225.