Communications

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

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Received August 20, 2002

Key Words: Carbonyl compounds, Hypervalent iodine, Microwave, Sulfonate

[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 $\alpha$-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 $\alpha$-organosulfonyloxy carbonyl compounds allows the enhanced simplicity of reactivity patterns and faster reaction rates when compared to $\alpha$-halo carbonyl compounds.3,4 In general, $\alpha$-halo carbonyl compounds have been used extensively as invaluable precursors in various organic transformations. However, the preparation of $\alpha$-halo carbonyl compounds are not straightforward and its toxic and unstable nature made their uses in organic transformations practically undesirable.5 Thus, the $\alpha$-organosulfonyloxy carbonyl compounds have been emerged as substitutes for $\alpha$-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 nosylate9 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 $\alpha$-[(2,4-dinitrobenzene)sulfonyl]oxy aromatic ketones, generated in situ from reaction of aromatic ketones with [hydroxy(2,4-dinitrobenzene-sulfonyloxy)iodo]benzene (HDNIB), readily converted to carboxylic acids in the presence of sodium peridote.10 In addition, very recently we have also reported a new reaction that dealt with efficient conversion of $\alpha$-[2,4-dinitrobenzene)sulfonyl]oxy cycloalkanones into dicarboxylic acid dimethyl esters using Oxone®.11 On the other hand, the reaction of $\alpha$-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 $\alpha$-[(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 $\alpha$-sulfonyloxyla...
ketones, cyclic ketones, and carbonyl compounds which include aliphatic ketones, aromatic
less than 6 h and the results are summarized in the Table 1.

A ketone (1.0 mmol) and HDNIB (0.562 g, 1.2 mmol) were
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 H2O and dried over MgSO4. 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. The microwave irradiation conditions proved
advantageous for
α-
[(2,4-dinitrobenzene)sulfonyl]oxylation
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
in a test tube and irradiated sequentially for 20–40 sec.

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R’</th>
<th>Yield (%)</th>
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<tbody>
<tr>
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<td>Me</td>
<td>H</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>Me</td>
<td>74</td>
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<tr>
<td>3</td>
<td>Ph</td>
<td>H</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>4-(Me)C6H5</td>
<td>H</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>4-(Cl)C6H5</td>
<td>H</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
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<td>90</td>
</tr>
<tr>
<td>8</td>
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</tr>
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*Isolated yields.