A convenient methodology for demercuration of organomercurials by Na/MeOH —
Synthesis of ethers

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Monoenes and dienes upon treatment with mercuric acetate in dry methanol, followed by demercuration with Na in methanol at 0°C, give ethers in good yields. The coagulation of mercury makes this a simple and convenient work-up process for such reactions.

The addition of mercuric salts, particularly mercuric acetate in dry solvents is a convenient procedure for the addition of mercury moiety and solvent across a C=C. This Markownikov’s addition is a simple method for functionalization of alkenes. The general procedure for the replacement of mercury by hydride ion is the treatment of the corresponding organomercurials with NaBH4/NaOH2-3, though, the literature records many other reducing reagents viz. potassium borohydride4,5, sodium trimethoxyborohydride6, calcium metal in methanol/THF7, Li, K, Mg/THF/anisidine8, N-benzyl-1,4-dihydronicotinamide9, sodium mercury amalgam10,11, alkaline hydrazine12-15 for demercuration of organomercurials. In an attempt to bifunctionalize the methoxy derivative of organomercurials, we found that mercury can be replaced very conveniently upon in situ treatment of methanolic solution of organomercurials with sodium metal. The whole one pot process involves the reaction of alkene with mercuric acetate in dry methanol at 0°C, followed by slow addition of sodium metal. The reaction procedure is simple as during this process mercury coagulates and the clear supernatant layer is decanted and after removal of methanol, residue is extracted with ether. The products are sufficiently pure for further use and chromatographic separation is needed only if detailed spectral analyses are required. We extended this methodology to dienes as a protocol of our chemoselective16 approaches (Eq. 1) and also to know the effect of Na/MeOH on the cyclopropyl ring and on another C=C present in the molecule. It has been found that both these moieties remain unharmed (Table I).

**Experimental Section**
Typical procedure. Hg(OAc)2 (1.59 g, 5 m mol) and dry methanol (20 mL) were stirred for 30 min at room temperature (= 30°C) in 50 mL round bottom flask under dry atmosphere of nitrogen. The flask was lowered to an ice-bath and 4-vinyl-1-cyclohexene (0.65 mL, 5 m mol) was added dropwise to the above vigorously stirred solution under nitrogen. The mixture was further stirred for 1 hr at 0°C and then

\[ \text{Hg(OAc)}_2/\text{MeOH},0^\circ\text{C} \rightarrow \text{HCO}_2 \]

\[ \text{(i)} \]

\[ \text{(ii)} \]

\[ \text{Na, } 0^\circ\text{C} \]

**Table 1 — Demercuration of organomercurials by NaMeOH to give ethers**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product*</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \text{-OCH}_3 )</td>
<td>( \text{-OCH}_3 )</td>
<td>89</td>
</tr>
<tr>
<td>2.</td>
<td>( \text{-OCH}_3 )</td>
<td>( \text{-OCH}_3 )</td>
<td>87</td>
</tr>
<tr>
<td>3.</td>
<td>( \text{-OCH}_3 )</td>
<td>( \text{-OCH}_3 )</td>
<td>91</td>
</tr>
<tr>
<td>4.</td>
<td>( \text{-OCH}_3 )</td>
<td>( \text{-OCH}_3 )</td>
<td>80</td>
</tr>
<tr>
<td>5.</td>
<td>( \text{-OCH}_3 )</td>
<td>( \text{-OCH}_3 )</td>
<td>82</td>
</tr>
<tr>
<td>6.</td>
<td>( \text{-OCH}_3 )</td>
<td>( \text{-OCH}_3 )</td>
<td>79</td>
</tr>
<tr>
<td>7.</td>
<td>( \text{-OCH}_3 )</td>
<td>( \text{-OCH}_3 )</td>
<td>81</td>
</tr>
</tbody>
</table>

*anti-Markownikov product was also formed in 7-16% yield. The ethers were identified by IR and NMR spectral analyses.
fine and dried cuttings of sodium metal (5 m mol, 120 mg) were added slowly at 0°C, over a period of 20 min. The stirring was continued for another 1 hr at 0°C which resulted into the coagulation of mercury. The clear supernatant layer was decanted from mercury, most of methanol was removed in vacuo and cold water was added to the residue which was then extracted with ether. The organic layer was washed with water (2×20 mL), brine (2×20 mL) and finally dried over Na2SO4. The evaporation of solvent under reduced pressure afforded the desired crude olefinic ether which was chromatographed over silica and eluted with EtOAc:pet. ether (1:9) to get the pure olefinic ether (82%).

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References