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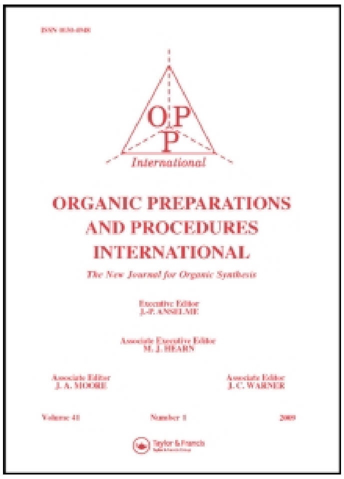

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# REDUCTIVE COUPLING OF CARBONYL COMPOUNDS TO PINACOLS WITH SAMARIUM/TMSCI SYSTEM

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# REDUCTIVE COUPLING OF CARBONYL COMPOUNDS TO PINACOLS WITH SAMARIUM/TMSCl SYSTEM

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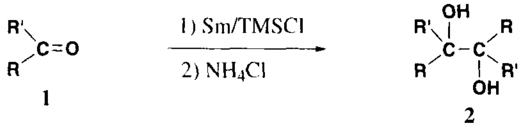
A number of systems have been developed for the preparation of pinacols from the reductive coupling of carbonyl compounds, *e. g.* magnesium,[1] aqueous titanium trichloride in basic media,[2] low valent cerium,[3] samarium diiodide,[4] and samarium diiodide-magnesium system.[5] The metal-trimethylsilylchloride (metal/TMSCl) system has stimulated great interest as a reductive system. Chan found that Mg/TMSCl in hexamethylphosphoramide is effective for the pinacol coupling.[6] Zinc is known to be activated by TMSCl in a variety of reactions including the Simmons-Smith cyclopropanation.[7,8] Furstner found that trimethylchlorosilane activated titanium(III) chloride and even commercial titanium powder in McMurry-type carbonyl coupling reactions.[9] Lautens reported trimethylchlorosilane as an activating agent in samarium-promoted cyclopropanation of allylic and a-allenic alcohols.[10] Herein we report the reductive coupling of carbonyl compounds to pinacols with the Sm/TMSCl system.



a) R = $C_6H_5$, R = H b) R = *p*-$ClC_6H_4$, R' = H c) R = *p*-$BrC_6H_4$, R' =H d) R = *p*-$CH_3C_6H_4$, R' = H e) R = *m*-$ClC_6H_4$, R' = H f) R = $C_6H_5$, R = $CH_3$ g) R = R' = $(CH_2)_5$ h) R = R' = $(CH_2)_4$

**Table 1**. Yields, mps. and $^1$H NMR Spectral Data of Pinacols (**2**)[a].

| Cmpd | Yield (%) | mp. (°C) | *lit.* mp. (°C) | Time (hrs) | dl:meso[b] | $^1$H NMR (δ) |
|---|---|---|---|---|---|---|
| 2a | 82 | 133-135 | 122-123 (dl)<br>139-140 (meso)[11]<br>134[12] | 4 | 58:42 | 2.95 (2H, s, OH), 4.43 (dl) and 4.60 (meso) (2H, s), 6.70-7.28 (m, 10H) |
| 2b | 90 | 149-151 | 109-110[12]<br>151[13] | 6 | 62:38 | 3.40 (2H, s, OH), 4.58 (dl) and 4.71 (meso) (2H, s), 6.80-7.43 (m, 8H) |
| 2c | 89 | 156-158 | 137-138[12] (from 95% ethanol) | 6 | 54:46 | 3.50 (2H, s, OH), 4.65 (dl) and 4.73 (meso) (2H, s), 6.86-7.45 (m, 8H) |
| 2d | 85 | 160-161 | 128 (hexane)[1]<br>145-146[15] | 5 | 50:50 | 2.18 (6H, s, $CH_3$), 3.15 (2H, s, OH), 4.46 (dl) and 4.55 (meso) (2H, s), 6.62-7.15 (m, 8H) |
| 2e | 88 | 141-143 | 96-98 (from benzene)[12] | 6 | 55:45 | 3.45 (2H, s, OH), 4.50 (dl) and 4.72 (meso) (2H, s), 6.78-7.45 (m, 8H) |
| 2f[c] | 76 | 117-119 | 120-123[1(b)] | 2 | 51:49 | 1.48 (dl) and 1.6 (meso) (6H, s, $CH_3$), 3.15 (2H , s, OH), 6.75-7.31 (m, 10H) |
| 2g[c] | 61 | 127-128 | 124.5-126.5[16] | 2 | / | 0.85-2.10 (m, 20H), 2.48 (2H , s, OH) |
| 2h[c] | 60 | 112-115 | 111.4-112.4[17] | 2 | / | 0.83-2.11 (m, 16H) 2.50 (2H , s, OH) |

a) At room temperature. b) Ratio determined by $^1$H NMR of protons. c) At reflux.

We found that aromatic aldehydes could be coupled to pinacols in good yields at room temperature. This pinacolic reductive coupling did not occur with ketones at room temperature but proceeded in reasonable yields (60-61%) under reflux. All compounds showed OH bond in the IR spectra. The results are summarized in *Table 1*.

In conclusion, it has been found that Sm/TMSCl system is an effective system for the pinacol coupling. The notable advantages of the present procedure are its mild and neutral conditions, simple operation and high yields.

## EXPERIMENTAL SECTION

Tetrahydrofuran was distilled from sodium/benzophenone ketyl immediately before use. Mps. were uncorrected. IR spectra were recorded on a Perkin-Elmer-683 spectrometer, $^1$H NMR spectra were obtained with a Bruker AC 80 spectrometer in $CDCl_3$ solution using TMS as internal standard.

**General Procedure**.- Samarium powder (0.45 g, 3.0 mg-atom), THF (20 mL) and trimethychlorosilane (0.65 g, 6 mmol) were added to a three-necked flask with stirring at room temperature under nitrogen. The aldehyde or ketone (2 mmol) was then added to the solution, and the mixture was stirred at room temperature for the indicated time. Saturated aqueous $NH_4Cl$ (10 mL) was added and the reaction mixture was extracted with ether (40 mL x 3). The ethereal solution was washed with water (40 mL x 3), and dried over $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The crude products were purified by preparative TLC on silica gel.

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# A NEW AND CONVENIENT SOLVENT-FREE METHOD FOR THE PREPARATION OF 1,4-DIARYLTHIOSEMICARBAZIDES

*Submitted by* (11/20/00)

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1,4-Disubstituted thiosemicarbazides exhibit a wide spectrum of biological activities, some having been used as anticollibacillus, antituberculosis, insecticides, herbicides and plant-growth regulator.[1-5] Generally, their synthesis have been carried out in solvent or using phase-transfer catalyst.[6-7] Although these methods have some merits, they also have drawbacks such as the use of large amounts of volatile and dangerous solvents, addition of expensive phase-transfer catalysts, need for heating and stirring apparatus. There is increasing interest in the use of environmentally benign reagents and conditions,[8-10] and particularly solvent-free procedures.[11-13] The many advantages include high efficiency and selectivity,[14] ease of isolation and purification, mild reaction conditions,[15] and environmental acceptability,[16,17] which are in keeping with the green requirements of energy-savings and high efficiency. Solvent-free procedures have been widely used in a variety of organic syntheses of substitution,[18] condensation,[19] oxidation-reduction,[20,21] rearrangement[22] and elimination.[23] However the solvent-free addition of aryl isothiocyanate and hydrazines has not been reported so far. We now report a new solvent-free route for the synthesis 1,4-disubstituted thiosemicarbazides.