Rapid Communication

Zinc-induced novel reductive cyclodimerisation of some α, β-unsaturated ketones

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Some α,β-unsaturated ketones are found to undergo zinc-induced novel reductive cyclodimerisation yielding substituted cyclopentanols as major products.

Recently, metal-mediated organic reactions in aqueous media have drawn considerable attention of synthetic organic chemists. The reported results of such reactions involving cheap and readily available zinc powder appear to be very interesting. The Zn-ZnCl₂-aq:THF induced coupling of ketones leading to 1,2-diols and Zn-AlCl₃·6H₂O-moist THF induced reduction of chalcones to dihydrochalcones encouraged us to study such reactions of E-3-arylideneflavanones, the synthesis and reactions of which are the subject matter of our current study. In this endeavour, E-3-benzylideneflavanone 1 was first subjected to a reaction condition somewhat similar to that used by Kanwar et al., when a product showing complicated 1H NMR spectral features than expected and M⁺ at m/z 626 was obtained. Realising that the product was formed through a novel coupling of two molecules of 1, we decided to study this reaction by taking more simple molecules as substrates. We also decided to perform the reaction by excluding AlCl₃ as there is no scope of the involvement of Al(0) owing to its position above zinc in the electrochemical series. A preliminary account of the interesting results obtained in this study is presented in this communication.

Three chalcones 2a-c were reduced with Zn/THF-H₂O (10:1) at room temperature. In each case two products were obtained. One was the novel cyclodimerisation product 3 and the other β,β-coupling product 4 (configuration undetermined).

Ytterbium was reported to be the first metal to effect the conversion 2a→3a, and recently, the ability of low-valent titanium (generated by treatment of TiCl₄ with zinc) to convert 2a to 3a and its C-1 epimer has become known. Our method, although giving 3 in only moderate yield, appears to be the most simple and inexpensive.

Table 1 — Zinc-induced reduction of some α, β-unsaturated ketones

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Product 3</th>
<th>Product 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar= Ph</td>
<td>Yield (%)</td>
<td>mp °C</td>
</tr>
<tr>
<td>2a</td>
<td>31</td>
<td>194-195</td>
</tr>
<tr>
<td>2b (Ar= 4-CH₃OC₆H₄)</td>
<td>34</td>
<td>157-158</td>
</tr>
<tr>
<td>2c (Ar= 3,4-OCH₃OC₆H₃)</td>
<td>35</td>
<td>195-196</td>
</tr>
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</table>
unsaturated ketones as substrates. The results will also be published in a future publication.

The products 3-5 are possibly formed through dimerisation of an initially formed radical anion 6 followed by changes in the resulting dianion by the routes as delineated in Scheme I. Our findings suggest that in the TiCl4-Zn-induced cyclodimerisation reactions, reported by Zhou et al.,7 the electron donating species may be either low-valent titanium or zinc or both. Attempts are being made to improve the yield of the products 3-5 and to evaluate the scope of the present reaction by involving more α,β-unsaturated ketones as substrates. The results will appear in a future publication.

In conclusion, we describe an extremely simple synthesis of substituted cyclopentanols using zinc dust, and this is an important addition to the list of very recent applications of this metal.8

Acknowledgement

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References and Notes


3. Colourless needles, mp 188-189°. Anal. Calcd for C12H10O2: C, 84.32, H, 5.47%. Found C, 84.06, H, 5.62%. IR (KBr): 3480 cm⁻¹ (C=O); 1H NMR (300 MHz, CDCl₃): δ 8.36 (1H, s, exchangeable with D₂O, OH), 3.29 (1H, dd, J = 12.4 and 8.2 Hz), 3.51 (1H, dd, J = 12.4 and 1.6 Hz). 3.62 (1H, d, J = 8.2 Hz), 5.20 (1H, d, J = 1.6 Hz), 5.67 (1H, d, J = 1.6 Hz), 5.61, 5.76 and 6.22 (each 1H, broad peak), 6.59-7.36 (22H, m), 7.55 (1H, d, J = 8.4 and 1.5 Hz), 8.07 (1H, dd, J = 8 and 1.7 Hz), 8.54 (1H, dd, J = 8 and 1.3 Hz); EIMS (rel int): m/z 626 (4.5%M'), 608 (1.5), 402(100), 314(100), 313(100), 282(19.7), 236(34.1), 224(96.4), 223(100), 193(100), 178(52.9), 121(100), 115(100) and 91(100).

4. Typical experimental procedure: To a well-stirred mixture of Zn dust (3.25g, 0.05 mole), THF (15mL) and water (2mL) a solution of an α,β-unsaturated ketone (0.01 mole) in THF (5mL) was added and the stirring continued at room temperature for 10 hr. The reaction mixture was poured into saturated NH₄Cl solution and extracted with ether. The residue obtained after removal of ether was subjected to column chromatography over silica gel when pure products were obtained.

5. (a) Melting point and spectral data of 3a were the same as reported. Spectral data of 3b and 3c were similar to those of 3a. (b) 4a: Anal. Calcd. for C₁₂H₁₀O₂: C, 86.09, H, 6.26%. Found C, 86.09, H, 6.26%. IR (KBr): 1690 cm⁻¹ (C=O); 1H NMR (300 MHz, CDCl₃): δ 2.93 (2H, dd, J = 16.8 and 2.7 Hz), 3.27-3.36 (2H, m), 3.73 (2H, dd, J = 4.1 and 3.0 Hz), 7.15-7.20 (2H, m), 7.27-7.48 (14H, m) and 7.63-7.67 (4H, m); EIMS (rel int): m/z 418(6.1) (M'), 400 (3.3), 327(2.7),
299(11.1), 298(39.1), 250(7.7), 223(2.3), 210(6.0), 209(13.7), 207(2.2), 206(2.3), 178(2.5), 130(2.0), 105(100) and 77(61.2). Compounds 4b and 4c gave similar spectral data.


