



Pergamon

Tetrahedron Letters 41 (2000) 2447–2448

TETRAHEDRON  
LETTERS

## Facile formation of the novel pyridyl substituted allene 2,4-bis(4-pyridyl)penta-2,3-diene

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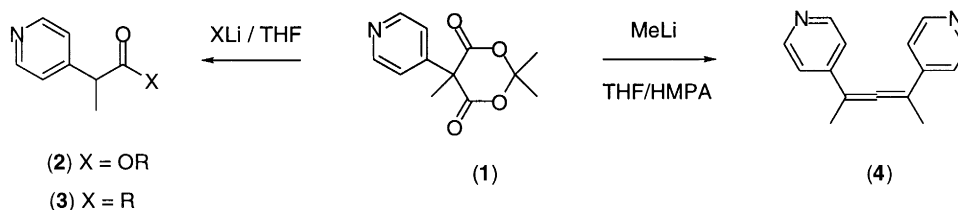
Received 25 November 1999; revised 13 January 2000; accepted 18 January 2000

### Abstract

Reaction of the Meldrum's acid derivative 2,2,5-trimethyl-5-(4-pyridyl)-4,6-dioxo-1,3-dioxane with methyl-lithium in THF/HMPA resulted in formation of the novel pyridyl substituted allene 2,4-bis(4-pyridyl)penta-2,3-diene. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* allenes; dioxanes; pyridines; rearrangements.

The 4-pyridyl substituted Meldrum's acid derivative 2,2,5-trimethyl-5-(4-pyridyl)-4,6-dioxo-1,3-dioxane **1** reacts with the lithium alkoxide of alcohols<sup>1</sup> to give the corresponding 2-(4-pyridyl)propanoate ester **2** (Scheme 1).



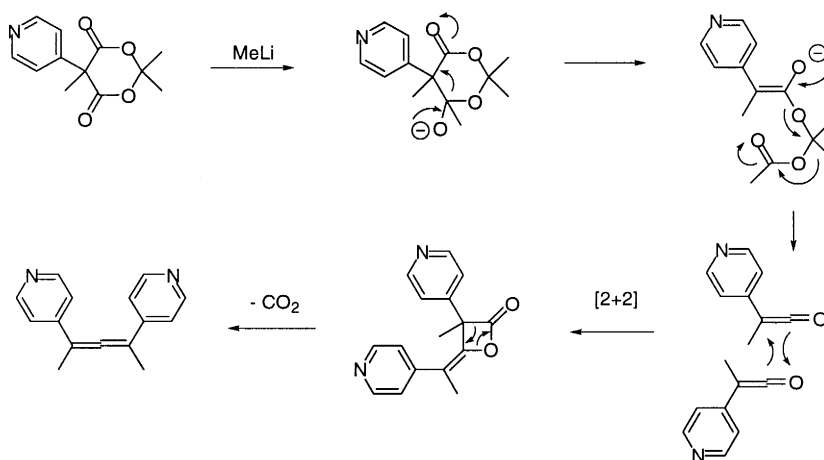
Scheme 1.

We sought to extend this reaction to provide a potentially useful route to pyridyl ketone analogues **3** by employing an organolithium reagent as a nucleophile. Accordingly **1** was treated with methyl lithium using THF as solvent, and the anticipated methyl ketone 3-(4-pyridyl)butan-2-one (**3a**, R=Me) was formed, but in low yield (16%). In an attempt to improve the yield of ketone formed, HMPA was added in order to enhance the nucleophilicity of the organolithium reagent. Interestingly, when this reaction was carried out at 0°C using HMPA as co-solvent (THF/HMPA=3:2), the novel allene, 2,4-bis(4-pyridyl)penta-2,3-diene **4** was formed as the major product in 73% yield,<sup>2</sup> together with only a small amount of the expected ketone **3a** (4%). The allene **4** had a very simple <sup>1</sup>H NMR spectrum showing only

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three separate signals, one methyl and two aromatic, due to the symmetry of the molecule. This allene has a C-2 axis of symmetry due to the perpendicularity of the central  $\pi$ -orbitals and is therefore chiral.<sup>3</sup>

Formation of this allene was a surprise, and how it is formed is mechanistically intriguing. Although this clearly involves dimerisation of an intermediate, a carbon atom must have been extruded to give the odd-numbered 3-carbon allenic unit. We have deduced a mechanism for formation of this allene that is consistent with literature precedent, and this is shown in Scheme 2. This mechanism involves generation of a ketene intermediate following attack of methyl lithium at the dioxodioxane ring carbonyl group. The resultant ketene then undergoes dimerisation via a [2+2] cycloaddition to give the  $\beta$ -lactone. This  $\beta$ -lactone intermediate then extrudes carbon dioxide to generate the allene. Literature precedent for this proposed mechanism is as follows. Meldrum's acid derivatives are known to generate ketenes, although this usually requires pyrolysis.<sup>4</sup> Ketenes are known to dimerise upon heating to produce stable  $\beta$ -lactones.<sup>5</sup> Pyrolysis of the  $\beta$ -lactone ketene dimer is also known to generate allenes.<sup>6</sup> Further support for this mechanism is the finding that tetraphenylallene is formed upon heating diphenylketene at 90°C in HMPA.<sup>7</sup>



Scheme 2. Proposed mechanism for generation of the allene **4**

What is remarkable here is that the pyridyl substituted allene **4** has been generated easily at low temperature, by a sequence of consecutive steps where the literature precedent for each step requires thermolytic conditions. We attribute the facility of the formation of **4** to the electron withdrawing ability of the 4-pyridyl ring.

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2. Preparation of 2,4-bis(4-pyridyl)penta-2,3-diene **4**. To a solution of **1** (3.53 g, 15.0 mmol) in THF (90 ml) and HMPA (60 ml), cooled to 0°C, was added methyl lithium (1.4 M in ether; 10.7 ml, 15.0 mmol). The reaction mixture was allowed to reach ambient temperature and stirred for 24 h. Ether/water work-up followed by chromatography, eluting with hexane:Et<sub>2</sub>O:Et<sub>3</sub>N (50:50:1), gave **4** as a yellow solid (2.43 g, 73%), mp 84–85°C. The product was air sensitive, and a green colour develops on prolonged exposure to air. IR  $\nu_{\max}$  1939, 1592 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.23 (6H, s, 2×CH<sub>3</sub>), 7.29 (4H, d, *J* 6.3 Hz, Py 3-*H* and 5-*H*), 8.56 (4H, d, *J* 6.3 Hz, Py 2-*H* and 6-*H*); *m/z* 222 (M<sup>+</sup>), 207, 144 (found: C, 80.83; H, 6.51; N, 12.52. C<sub>15</sub>H<sub>14</sub>N<sub>2</sub> requires C, 81.05; H, 6.35; N, 12.60).
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