

## Perkin Communications

### A New Method for the Preparation of 1,5-Dicarbonyl Compounds from Bicyclic Ketals

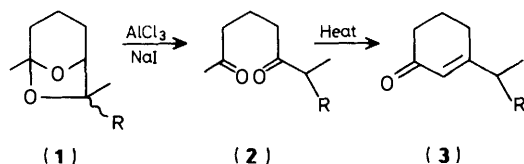
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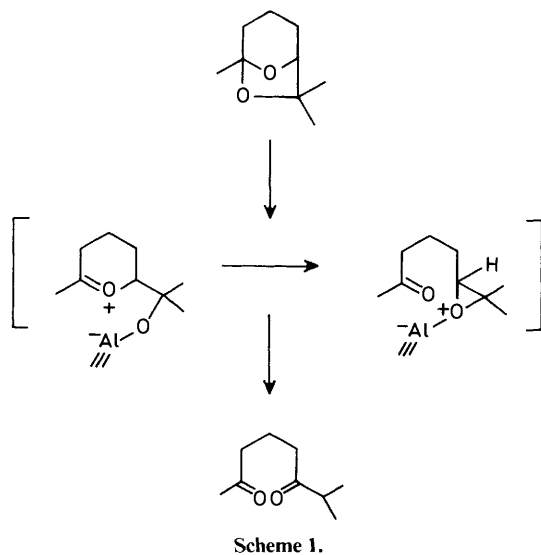
1,5-Dicarbonyl compounds have been prepared from bicyclic ketals in high yield under mild conditions by using aluminium chloride–sodium iodide in methylene dichloride.

Although Lewis acid induced rearrangements of bicyclic ketals are an attractive method for the synthesis of natural products,<sup>1</sup> they have been little investigated. In our studies of the 6,8-dioxabicyclo[3.2.1]octane skeletal system<sup>2</sup> which is easily prepared from methyl vinyl ketone,<sup>3</sup> we have found a new synthetic route from bicyclic ketals to 1,5-dicarbonyl compounds, with potential as intermediates for 6-membered heterocycles<sup>4</sup> and cyclopentane derivatives.<sup>5</sup>

Mild reagent systems such as boron trifluoride–diethyl ether–sodium iodide,<sup>6</sup> chlorotrimethylsilane–sodium iodide<sup>7</sup> and aluminium chloride–sodium iodide<sup>8</sup> were used to cleave the bicyclic ketal with interesting results.

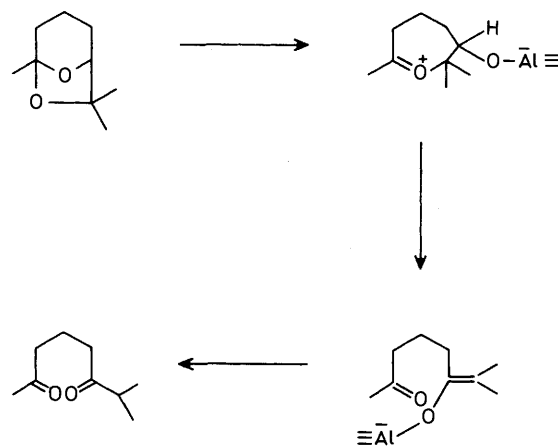


A solution of 5,7,7-trimethyl-6,8-dioxabicyclo[3.2.1]octane (**1a**) in methylene dichloride reacted during 3 h at ambient temperature with aluminium chloride (2 equiv.)–sodium iodide (2 equiv.) to give, after basic work-up followed by short-path column chromatography, the 1,5-diketone (**2a**) (71%). This is a novel rearrangement which could involve a 1,2-hydrogen shift *via* an epoxide intermediate (see Scheme 1). All of our previous



Scheme 1.

experience had been specifically directed towards the O(6)–C(5) bond as a way to prepare pyran rings from the bicyclic ketals. The specificity of this cleavage can be seen in the reductive cleavage of (**1a**) with acetyl iodide,<sup>2</sup> and with aluminium hydride.<sup>9</sup> Although it has been established that O-6 is the preferred site of lanthanide interaction during lanthanide-induced shift studies,<sup>10</sup> O-8 preference cannot be eliminated as an alternative mechanism (see Scheme 2). Further studies into this mechanism are currently underway in our laboratory.



Scheme 2.

In the reaction with boron trifluoride–diethyl ether–sodium iodide, a mixture of (**2**) and cyclohexenone (**3**) was obtained, the ratio of which varied with time.† Only (**3**), with other unidentified products, was produced in the reaction with chlorotrimethylsilane–sodium iodide. All of (**2**) was also converted into (**3**), by intramolecular aldol condensation, when submitted to g.c. Interestingly, aluminium chloride–sodium iodide in methylene dichloride at room temperature produce

† Spectral data for (**2a**):  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 200 MHz), 1.09 (6 H, d, *J* 7.2 Hz, 2 × Me), 1.83 (2 H, p, *J* 7.0 Hz, CH<sub>2</sub>), 2.13 (3 H, s, COMe), 2.46 (2 H, t, *J* 7.0 Hz, COCH<sub>2</sub>), 2.49 (2 H, t, *J* 7.0 Hz, COCH<sub>2</sub>), and 2.58 (1 H, m, CH);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>), 17.8 (t), 18.2 (q, 2 × Me), 29.8 (q), 39.0 (t), 40.8 (d), 42.6 (t), 208.4 (s), and 214.2 (s);  $\nu_{\text{max}}$ (neat) 1709br (C=O) cm<sup>-1</sup>; for (**3a**)  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 200 MHz), 1.05 (6 H, d, *J* 7 Hz, 2 × Me), 1.97 (2 H, m, CH<sub>2</sub>), 2.33 (5 H, m, 2 × CH<sub>2</sub> and CH), and 5.83 (1 H, s, CH=);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>), 21.1 (q, 2 × Me), 23.5 (t), 28.2 (t), 36.2 (d), 38.1 (t), 124.0 (d), 172.4 (s), and 200.7 (s);  $\nu_{\text{max}}$ (neat) 1667s (C=O) and 1634w (C=C) cm<sup>-1</sup>. Compounds (**2b–e**) were also characterized by <sup>1</sup>H n.m.r. and i.r. spectroscopy.

**Table.** Preparation of 1,5-dicarbonyl compounds (**2**)

Entry	R	Time (h)	% Yield (isolated)
<b>a</b>	Me	3	71
<b>b</b>	Pr	3	91
<b>c</b>	Pr <sup>i</sup>	3	86
<b>d</b>	Ph	1.5	43
<b>e</b>	H	3	74

only (**2**) in high yield, but the reagent system in acetonitrile as solvent gives no reaction at room temperature and only (**3**) at reflux. Aluminium iodide (prepared from aluminium foil and iodine),<sup>11</sup> yielded a mixture of (**2**) and (**3**). It seems that aluminium chloride-sodium iodide which was used for ether cleavage by Node *et al.*<sup>8</sup> is much milder and more effective for ketal cleavage. The Table shows the generality of this method in terms of substitution pattern.

#### Acknowledgements

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