

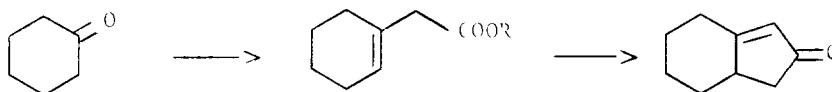
A New Approach to Simple Cyclopentenones  
Application to the Synthesis of Dihydro and *cis*-Jasmone

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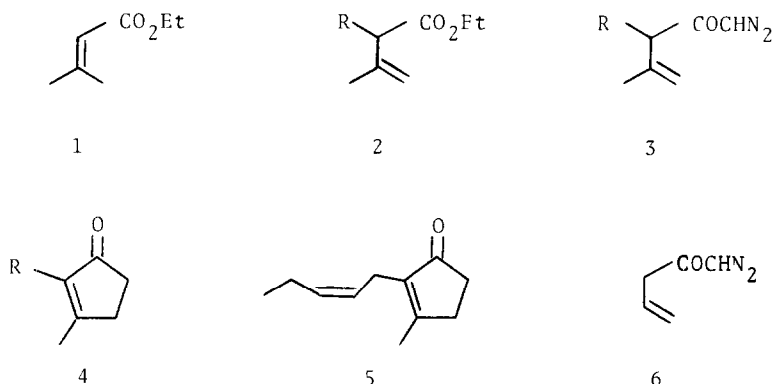
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During the course of our exploratory studies<sup>1</sup> on the chemistry of  $\beta,\gamma$ -unsaturated diazomethyl ketones, we recently devised, through the agency of  $\text{BI}_3 \cdot \text{Et}_2\text{O}$  in nitromethane, a new synthesis of the cyclopentenone ring which in conjunction with the now improved approaches to  $\beta,\gamma$ -unsaturated acids<sup>2</sup> leads to an efficient cyclopentenone annelation method<sup>3</sup>



We now wish to draw attention to the utilization of  $\beta,\gamma$ -unsaturated diazoketones for the preparation of simple cyclopentenones including dihydro- and *cis*-Jasmone<sup>4</sup>. Alkylation and/or deconjugation of 3,3-dimethyl acrylic acid ethyl ester (1) with methyl iodide, n-pentyl bromide or 1-bromo-2-pentyne in THF,

employing as base the lithium diisopropylamide hexamethylphosphoramide complex described recently by Rathke<sup>5</sup> and Schlessinger,<sup>6</sup> gave esters (2a-d)<sup>7</sup> in 72-94%<sup>8</sup>



Yield (1 → 4)

a) R = H	37 %
b) R = CH <sub>3</sub>	24 %
c) R = C <sub>5</sub> H <sub>11</sub>	43 %
d) R = CH <sub>2</sub> C≡CCH <sub>2</sub> CH <sub>3</sub>	34 %

Subsequent careful hydrolysis under conditions which prevented conjugation [1 l mixture of 15% NaOH and EtOH, 25°, 18 hrs] led to the corresponding β,γ-unsaturated acids which were converted to the desired diazoketone (3a-d) in an overall yield of 70-85% via the standard acid chloride-diazomethane procedure<sup>9</sup> In each case examination of the intermediate acid and acid chloride derivative by ir and nmr documented the presence of an isopropenyl group Cyclization was then effected exclusively to cyclopentenones (4a-d) in 40-65% yield by treatment of (3a-d) at 0° in dry nitromethane for 15 min with 1 l eq of BF<sub>3</sub>·Et<sub>2</sub>O, followed by addition of 10% aq HCl and heating at reflux for 2 hrs<sup>10</sup> Structures of cyclopentenones (4a-c) were confirmed by comparison with authentic samples, whilst (4d) yields a known 2,4-dinitrophenylhydrazone (mp 165-166°, Lit<sup>11</sup> mp 166°) Subsequent hydrogenation of (4d) over Lindlar catalyst lead in near quantitative yield to cis-Jasmone (5) identical with an authentic sample



## REFERENCES AND FOOTNOTES

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- 8 Yields were determined by g l c calibration and are not maximized
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