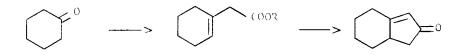
A New Approach to Simple Cyclopentenones Application to the Synthesis of Dihydro and cis-Jasmone

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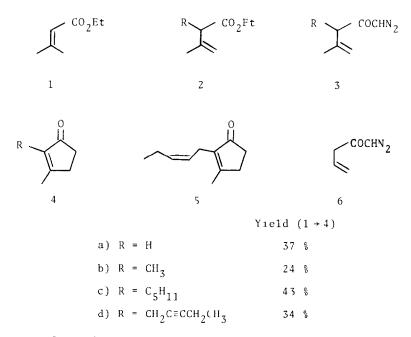
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During the course of our exploratory studies<sup>1</sup> on the chemistry of  $\beta,\gamma$ -unsaturated diazomethyl ketones, we recently devised, through the agency of Bl<sub>3</sub> Ft<sub>2</sub>0 in nitromethane, a new synthesis of the cyclopentenone 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>

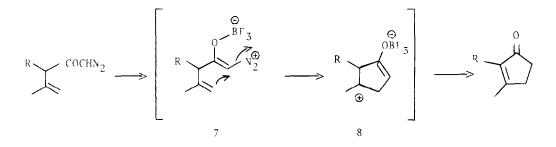


We now wish to draw attention to the utilization of  $\beta$ ,  $\gamma$ -unsaturated diazoketones for the preparation of simple cvclopentenones including dihydro- and  $\zeta_1 \xi$ -Jasmone<sup>4</sup> Alkylation and/or deconjugation of 3,3-dimethyl acrylic acid ethyl ester (1) with methyl iodide, 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  $(2a-d)^7$  in 72-94%<sup>8</sup>



Subsequent careful hydrolvsis under conditions which prevented conjugation [1 1 mixture of 15% NaOH and EtOH, 25°, 18 hrs] led to the corresponding  $\beta,\gamma$ -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 1 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°, Lii<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 A reasonable pathway for the cyclization of (3a-d) involves  $BF_3$  complexation presumably at oxygen of the diazoketone (eg 7) followed by intramolecular  $\pi$ -bond participation in the displacement of nitrogen thereby leading to tertiary carbocation (8) Subsequent elimination of a proton and treatment with aqueous acid vields the respective cyclopentenones This cyclization is an extension of the acid-catalyzed intramolecular carbon-alkylation of  $\beta,\gamma$ -unsaturated diazoketone recently introduced by Mander<sup>12</sup> and Erman<sup>13</sup>, and represents a new cyclopentenone synthesis



To explore the generality of this approach to simple cyclopentenones, diazoketone (6), which would be expected to proceed via a less stable secondary carbocation, was subjected to our cyclization procedure. In that event cyclopentenone, identical in all respects with an authentic sample, was isolated albeit in only 13% yield. This observation demonstrates that a major but not limiting driving force in the cyclization of  $\beta,\gamma$ -unsaturated diazoketones is the formation of a stable cationic intermediate. Studies on both the synthetic and mechanistic aspects of this transformation are continuing in our laboratory

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