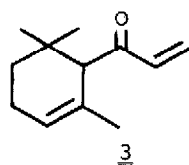
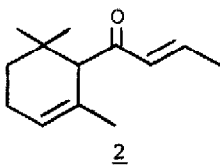
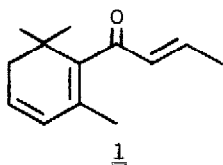


A TOTAL SYNTHESIS OF  $\alpha$ -DAMASCONES

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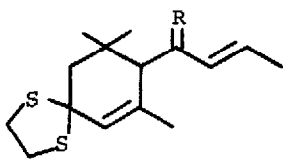
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Since  $\beta$ -damascenone (1) was first isolated from Bulgarian rose oil<sup>1</sup>, extensive attention<sup>1-10</sup> has been drawn to the preparation of this odoriferous enone as well as to that of its related compounds which are of equal industrial interest. The existing syntheses of trans- (2) and cis- $\alpha$ -damascone (3) involve modifications of  $\alpha$ -cyclocitral<sup>1</sup> or  $\alpha$ -ionone<sup>2,6-8</sup>. We wish to report an efficient total synthesis of  $\alpha$ -damascenes without relay.



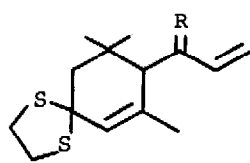
The starting keto ester 4 was prepared by boron trifluoride catalyzed condensation of ethyl acetoacetate with acetone according to the procedure of Rubinstein<sup>11</sup>. This reaction gave, in our hands, a mixture of 4 and its positional isomer 5<sup>12</sup> in a ratio of ca. 2:1. The two isomers could be separated by extensive column chromatography and 4, upon treatment with 1,2-ethanedithiol and boron trifluoride etherate, gave thioketal ester 6 in near quantitative yield. In a more convenient procedure, the mixture of 4 and 5 was subjected directly to the thioketalization without the laborous separation. At 0° for 7 hr., 4 reacted with 1,2-ethanedithiol exclusively and completely to give 6 whereas 5 remained totally unreacted.





9 R=OH, H

11 R=O



10 R=OH, H

12 R=O

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#### References and Footnotes

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16. The isomerization most likely occurred prior to the oxidation since further treatment of 12 with manganese dioxide under the same conditions did not produce any detectable amount of 11.
17. At present we are unable to effect the desulfurization without partial isomerization of the double bond.