

A NOVEL "LINCH-PIN" CONSTRUCTION OF DIHYDROJASMONE

A HIGH YIELD SYNTHESIS OF *CIS*-JASMONE

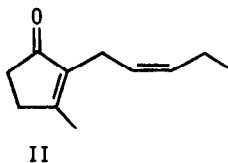
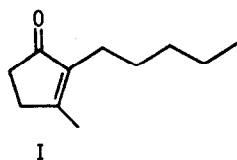
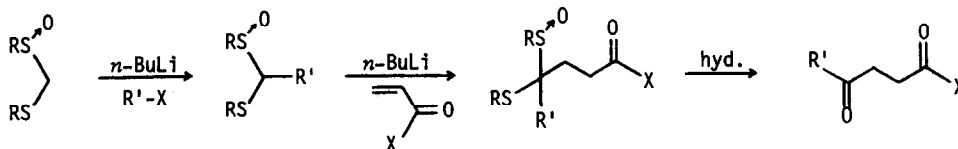
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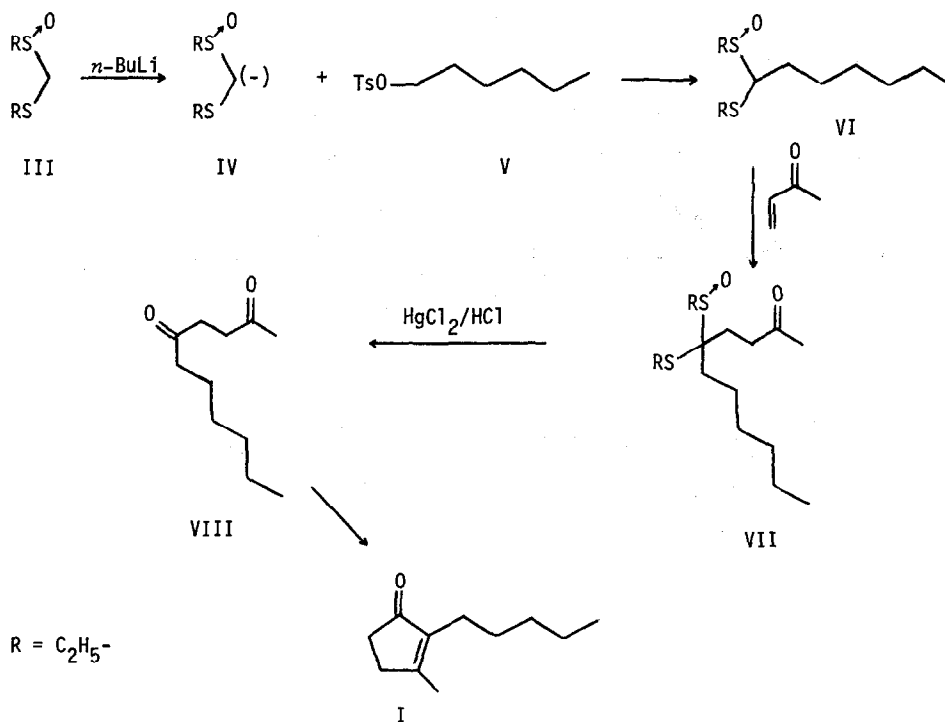
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We have outlined in the preceding communications the alkylation¹ and conjugate addition² behavior of a new class of carbonyl anion equivalents. The development of these synthetic reactions allows the assemblage of 1,4-dicarbonyl compounds wherein the carbonyl anion equivalent is incorporated into these systems as the "linch-pin" component *via* the simple alkylation-conjugate addition sequence shown below. In order to further demonstrate the efficiency of this synthetic strategy, we have carried out syntheses of dihydrojasmone (I) and *cis*-jasmone (II) and herein wish to report the details of this experimental effort.³

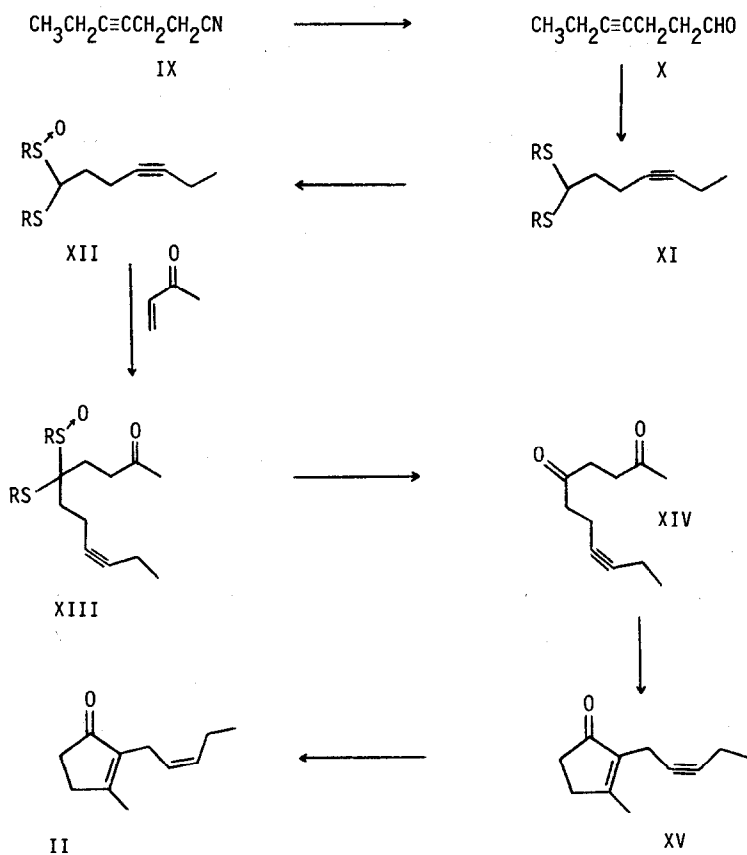


Dihydrojasmane. A "linch-pin" synthesis of I has been realized in 74% overall yield starting from the thioacetal monosulfoxide III¹ and the tosylate of *n*-hexanol V.⁴ Sulfoxide III (1 equivalent, 1 molar in THF) was converted into its corresponding anion IV by treatment at 0° with *n*-butyllithium (1 equivalent). After stirring for 15 minutes, the tosylate V (1 equivalent) dissolved in hexamethylphosphoramide (1 equivalent) was added to the anion and the resulting mixture was stirred 12 hours at 0°. Work-up in the usual manner with saturated ammonium chloride gave the substituted sulfoxide VI (bp 110°, 5×10^{-3} torr) in 95% yield.⁵ Alternatively, this sulfoxide can be prepared in two steps from heptanal (85% overall yield).⁶

Using conditions already described,² sulfoxide VI (1 equivalent) was reacted with methyl vinyl ketone (1 equivalent) to give the conjugate addition product VII. This material, without purification, was hydrolyzed in the presence of mercuric chloride¹ to give the dione VIII (bp 95°, 0.5 torr) in 90% yield. Lastly, cyclization of VIII with ethanolic sodium hydroxide gave dihydrojasmane (I)⁷ in 85% yield, thereby completing a highly efficient "linch-pin" construction of this cyclopentenone derivative.



***cis*-Jasmone.** 4-Heptynonitrile (IX)⁸ has been transformed into *cis*-jasmone (II) in 63% overall yield. Nitrile IX was reduced at -55° with diisobutylaluminum hydride in hexane to the aldehyde X which without isolation was converted into the thioacetal XI (bp 82° , 0.08 torr) in 92% overall yield. Oxidation of XI with sodium meta-periodate in aqueous methanol afforded the monosulfoxide XII (90%, bp 117° , 5×10^{-3} torr). Michael addition of XII (1 equivalent) to methyl vinyl ketone (1 equivalent) gave the adduct XIII. Compound XIII (crude) was hydrolyzed with a catalytic amount of 70% perchloric acid in ether solution to the dione XIV⁹ (96%, bp 73° , 1×10^{-3} torr). The dione XIV was converted in 90% yield into 2', 3'-dehydrojasmone XV (2,4-DNP, mp 164° ; lit¹⁰ 165°) by treatment with dilute ethanolic sodium hydroxide.¹¹ Completion of the synthesis was accomplished by reduction of XV using Lindlar catalyst to give uncontaminated *cis*-jasmone in 92% yield (2,4-DNP, mp 116° ; lit¹² 116°).



Clearly, the novel and efficient assemblage of 1,4-dicarbonyl compounds possible with this new class of carbonyl anion equivalents should be of continuing significance in organic synthesis.

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REFERENCES

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2. J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *ibid.*, in press.
3. For an extensive compilation of existing syntheses of these compounds, see H. C. Ho, T. L. Ho, and C. M. Wong, *Can. J. Chem.*, **50**, 2718 (1972).
4. A. M. Cohen, A. H. Somny, and J. S. Penne, *Bull. Chim. Soc. France*, **32**, 711 (1965).
5. The yields given for all reactions are for isolated products. All compounds exhibited satisfactory spectral and physical properties.
6. An outline of the experimental procedure used for this two step transformation is given in reference 1.
7. Dihydrojasmane prepared in this manner exhibited the same spectral and physical properties as those reported in reference 3.
8. M. F. Ansell, J. C. Emmett, and R. V. Coombs, *J. Chem. Soc., C*, 217 (1968). A "linch-pin" construction of *cis*-jasmane was not attempted after it was found that the tosylate of 3-hexyn-1-ol did not undergo alkylation with the anion V but rather gave predominantly the corresponding elimination product.
9. J. E. McMurry, and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971).
10. K. S. Sido, Y. Kawasima, and T. Isida, *Perfum. Essent. Oil Rec.*, **57**, 364 (1966).
11. The cyclization procedure used was that described in reference 3.
12. *cis*-jasmane prepared in this manner exhibited the same spectral and physical properties as those reported in reference 3.