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# MELDRUM'S ACID DERIVATIVE AS A USEFUL DIENOPHILIC COMPONENT; SYNTHESIS OF δ-DAMASCONE[1]

William G. Dauben, Alan P. Kozikowski,[2] and William T. Zimmerman
Department of Chemistry, University of California
Berkeley, California 94720

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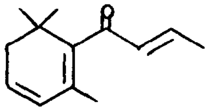
Since 1970 when β-damascenone (1) was reported as a fragrant ketone in Bulgarian rose oil,[3] the preparation of it and compounds related to it has been actively pursued.[4-7] In these studies, δ-damascone (2), a dihydroisomer with a strong, pleasant, rose odor similar to that of 1, has been synthesized[6,7] and we should like to report yet another synthesis of 2 which is efficient and simple and which is based on the utility of isopropylidene isopropylidenemalonate (4) as a dienophile.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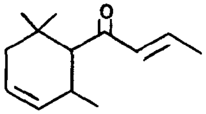
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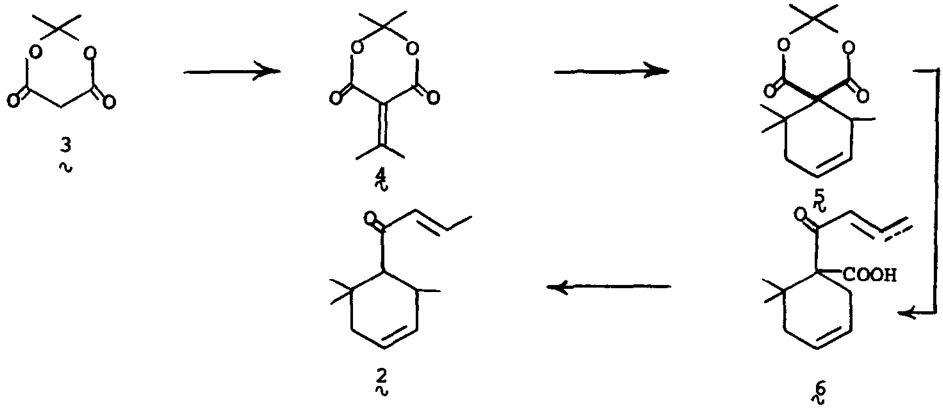
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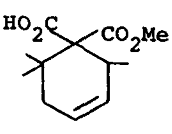
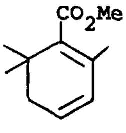
6
2

Isopropylidene malonate (**3**), called Meldrum's acid and prepared from malonic acid and acetone in acetic anhydride and sulfuric acid in 50% yield[8], was condensed again with acetone in the presence of pyridine and molecular sieves (type 4A) to give isopropylidene isopropylidenemalonate (**4**) in 54% yield.[9] The ester **4**, serving as a dienophile, was allowed to react with an excess of 1,3-pentadiene at 130° for 12 hr to yield the cyclic adduct **5** in 66% yield. This result is in contrast to the reported nonreactivity of dimethyl isopropylidenemalonate with 1,3-pentadiene under a variety of conditions.[7] Treatment of **5** with allyllithium gave a mixture of keto-acid **6** (α,β and β,γ isomers) and δ-damascone **2**; the sidechain double bond was brought into conjugation by heating the mixture with $NH_4Cl$ in THF. The conjugated mixture could be separated and both components purified but it was found advantageous to the final yield of **2** to decarboxylate first the remaining β-keto acid. The crude mixture was heated at 165° for 2 hr, extracted with dilute NaOH,[10] and the neutral oil distilled [bp 61-64° (0.3mm)] to give δ-damascone (**2**) in 66% yield from adduct **5**.

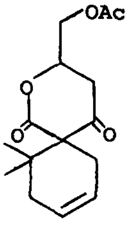
The versatility of **4** as a dienophile was shown by its ability to function as a masked half ester of a dicarboxylic acid in the Diels-Alder reaction, and, thus in the present study be employed to prepare potential intermediates to β-damascenone, itself. Treatment of **5** with methanolic sodium methoxide at room temperature yielded half ester acid **7** in nearly quantitative yield. Several attempts to convert this latter material to methyl safranate (**8**), an



**7**



**8**



**9**

intermediate in reported damascenone syntheses, by oxidative decarboxylation procedures, failed to yield any single product in high yield. Treatment of the β,γ isomer of **6** with $Pb(OAc)_4/I_2$ only yielded **9** by acetoxylactonization.

## REFERENCES AND FOOTNOTES

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2) National Science Predoctoral Fellow, 1971-1974.
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10) This alkaline wash is essential to remove polyphenols which are solids and which slowly precipitate from distilled material. These polyphenols are formed by Claisen rearrangement and condensation of residual allyl phenyl ether used to prepare allyllithium.