Preparation of Derivatives of Tricyclo[4.2.0.$0^{1,4}$]octane, Broken Window Compounds

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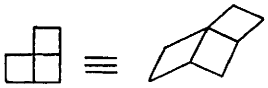
Summary Photolysis of 3-(3-methylbut-3-enyl)cyclopent-2-enone (**4**) leads to the tricyclo[5.2.0.$0^{1,5}$]nonane (**5**); the derived diazoketone (**7**) undergoes Wolff rearrangement to give esters (**8**) and (**9**), derivatives of tricyclo[4.2.0.$0^{1,4}$]octane (**1**).

THE unreported hydrocarbon tricyclo[4.2.0.$0^{1,4}$]octane (**1**) has been called[1] [4.4.4]fenestrane and a broken window in recognition of a formal relationship with its tetracyclic homologue (**2**). This latter compound, known as [4.4.4.4]-fenestrane[1] or simply fenestrane,[2] has been the object of several recent discussions and much synthetic interest.[3] We now report the preparation of derivatives of (**1**) by a route extending our recent observation that in 1,5-hexadien-3-ones (**3**) alkyl substitution at C(5) [R in (**3**)] enhances 1,6-cyclization in intramolecular photochemical cycloaddition reactions.[4]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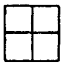
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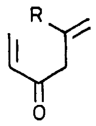
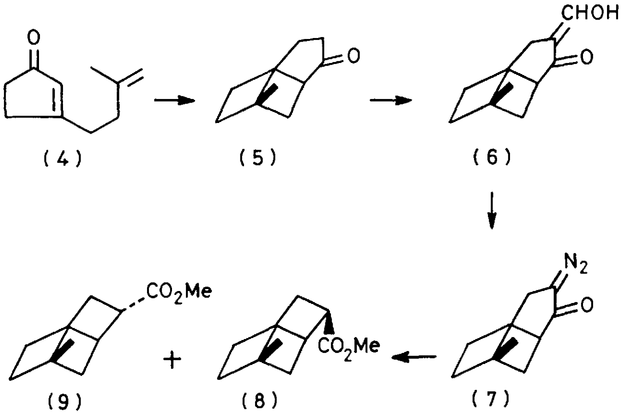


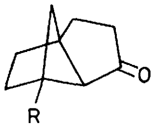
(3)

The synthesis is summarized in the Scheme. The substituted cyclopentenone (**4**) was available through addition of isopentenylmagnesium bromide to cyclopentenone followed by oxidative rearrangement of the intermediate allylic alcohol.[5] As anticipated from our earlier results,[4] photolysis (λ >330 nm) of the cyclopentenone (**4**) in benzene yielded (**5**) (67%) as the major product. This structural assignment and particularly the conclusion that the product is (**5**) and not the alternative crossed cycloadduct

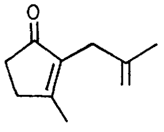
(**10**) rest on the following considerations. Thermolysis of (**5**) in benzene at 160 °C for 10 h gave virtually quantitatively a mixture of (**4**) (98%) and (**11**) (2%).[6] This pyrolysis is expected[7] to lead to biradical (**12**) which can then open to (**4**) or (**13**). Subsequent conjugation of the double bond in (**13**) would give (**11**). A control experiment showed that (**4**) is stable to the pyrolysis conditions; we conclude that (**11**) is a direct product from (**5**) and not the result of subsequent Cope rearrangement of (**4**). The crossed adduct (**10**) could open to (**4**) but not directly to (**13**) or (**11**). The 600 MHz n.m.r. spectra of (**5**) and its trideuterio-derivative obtained on base-catalysed exchange are quite different from the spectrum of cycloadduct (**14**) formed on photolysis of 3-(but-3-enyl)cyclopent-2-en-1-one.[8] Further, irradiation of (**5**) (λ >280 nm) in benzene–methanol furnished the α-cleavage product (**15**) and not its isomer (**16**). These assignments make use both of the well-documented differences between the n.m.r. spectra of bicyclo[2.2.0]hexanes[9] and the isomeric bicyclo[2.1.1]-hexanes,[10] and also of the fact that bicyclo[2.2.0]hexanes undergo pyrolytic fragmentation at lower temperatures (*ca.* 130—175 °C)[11] than do bicyclo[2.1.1]hexanes (*ca.* 330—375 °C).[12]



Scheme.



(10) R = Me
(14) R = H



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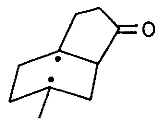

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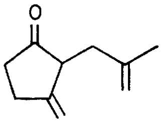

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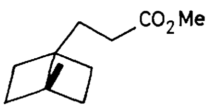

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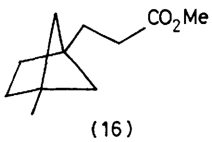

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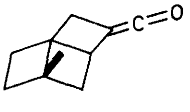
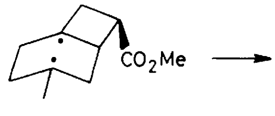


(17)

Reaction[13] of (**5**) with methyl formate and base furnished the crystalline α-hydroxymethylene ketone (**6**), and treatment[14] with tosyl azide then gave (**7**). On irradiation in methanol, diazoketone (**7**) underwent photochemical Wolff rearrangement[15] to a mixture of the two methyl esters (**8**) (*ca.* 68%) and (**9**) (*ca.* 12%).

Esters (**8**) and (**9**) arise through addition of methanol to the keten (**17**), and preferential formation of (**8**) through attack from the less hindered side has good precedent.[16] In keeping with this assignment, treatment of the major ester (**8**) with methanolic sodium methoxide led to >90% inversion to its more stable isomer (**9**). Use of MeOD in the Wolff rearrangement furnished the α-deuterio esters, which were useful in interpretation of the n.m.r. spectra of (**8**) and (**9**). The structures of these esters rest not only on spectroscopic data, but also on the pyrolysis of each ester at 190 °C in benzene to give three products in overall essentially quantitative yield. From (**8**) these products are (**19**) (78%), (**21**) (17%), and (**22**) (5%), which can be accounted for as follows. Thermolysis[7] of (**8**) leads exclusively to the bis-tertiary biradical (**18**), which fragments in both possible senses, forming (**19**) and (**20**).



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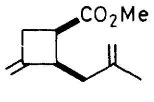

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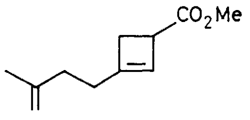

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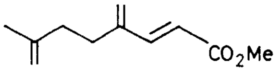

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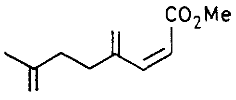

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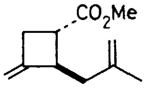

(23)

Cyclobutene (**20**) undergoes secondary thermal conrotatory opening to give mainly the expected[17] (*E*)-substituted ester (**21**) plus a small amount of the (*Z*)-isomer (**22**). The ratio (**22**):(**21**) decreased at lower reaction temperatures. A similar scheme can be written for fragmentation of the isomeric ester (**9**); here the pyrolysis products are (**23**) (74%), (**21**) (23%), and (**22**) (3%).

All new compounds have spectroscopic properties fully compatible with the structures assigned. All except (**7**) were further characterized by acceptable elementary analysis for carbon and hydrogen or by the appropriate molecular ion in the high resolution mass spectrum.

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