Synthesis of Methyl 1-Methyltetracyclo[4.3.1.$0^{3,10}$.$0^{8,10}$]decane-7-carboxylate, a Derivative of [4.4.4.5]Fenestrane

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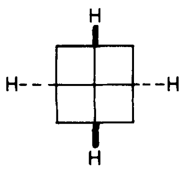
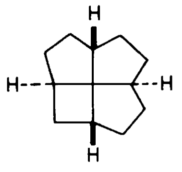
Photolysis of dienone (**7**) furnishes (**9a**), which by way of the diazoketone (**12**) is cyclized to the difunctionalized [4.4.5.5]fenestrane (**13**); conversion into (**17**) and subsequent Wolff rearrangement gives (**18a**) and (**18b**); the latter, major isomer is the first [4.4.4.5]fenestrane to be characterized.

Synthetic efforts in recent years have led to the preparation of several ring systems related to the unknown but much discussed[1] tetracyclo[3.3.1.0.^{3,9}0^{7,9}]nonane (**1**) ([4.4.4.4]-fenestrane, windowpane). There are known representatives of the [4.5.5.5]- (**2**),[2,3] [4.4.5.5]- (**3**),[2] [5.5.5.5]- (**4**),[4] and [4.4.4]- (**5**)[5,6] fenestranes, as well as homologous tetracyclic systems composed of larger rings.[7] Interest in these systems arises from the severe strain and distortion expected at the central quaternary carbon atom of (**1**). Our exploration of routes to (**1**) has now led to derivatives of tetracyclo[4.3.1.$0^{3,10}$.$0^{8,10}$]decane (**6**) ([4.4.4.5]fenestrane), the smallest and most strained tetracyclic fenestrane to be synthesized to date. The approach employed is grounded in our earlier route to (**5**) and its derivatives;[6] details are given below.

The starting keto ester (**7**) was available following a procedure for related compounds.[8] In the same manner as earlier intramolecular cycloaddition of (**8**),[6] photolysis ($\lambda > 340$ nm, hexane solution) of (**7**) furnished (84%) a *ca.* 2 : 1 mixture of the desired (**9a**) together with the epimeric ester (**9b**). Equilibration served to establish the stereochemistry of these esters; the more hindered (**9b**) is largely inverted to (**9a**) on treatment with base, and at equilibrium the ratio (**9a**) : (**9b**) is *ca.* 2 : 1. The derived acetal (**10**) was then converted by way of acid (**11**) and the related acyl chloride into the diazoketone (**12**). Treatment of (**12**) with rhodium(II) acetate[9] in dichloromethane caused rapid decomposition and formation of the tetracyclic ketone acetal (**13**) [64% from (**11**)]. Similar decomposition of the epimeric diazoketone prepared analogously from (**9b**) yielded no product corresponding to (**13**). Models indicate that only the ketocarbene from (**9a**) should insert to form the [4.4.5.5]fenestrane system and that this reaction should yield the stereochemistry depicted in (**13**). In support of this latter conclusion (**13**) was reduced to the symmetrical hydrocarbon (**14**). Deacetalization of (**13**), treat-



(1)



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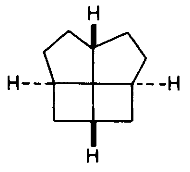

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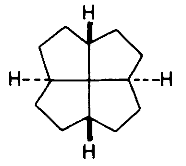

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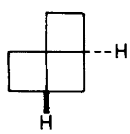

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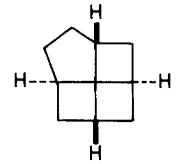
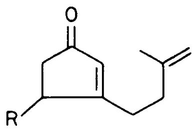
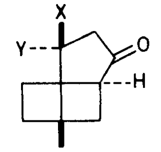


(6)



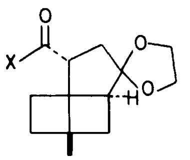
(7) R = CO$_2$Et

(8) R = H



(9) a; X = H, Y = CO$_2$Et

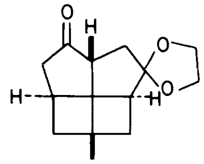
b; X = CO$_2$Et, Y = H



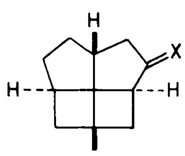
(10) X = OEt

(11) X = OH

(12) X = CHN$_2$

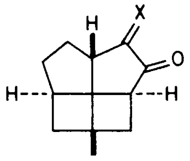


(13)



(14) X = H$_2$

(15) X = O

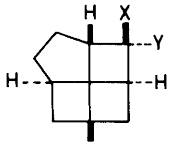


(16) X = CHOH

(17) X = N$_2$

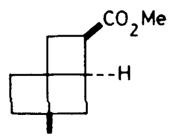
ment with lithium aluminium hydride to give the diol, and then further hydride reduction of the derived ditoluene-*p*-sulphonate furnished the methyl[4.4.5.5]fenestrane (**14**). As required by symmetry, the ^{13}C n.m.r. spectrum of (**14**) consists of only eight lines.

A similar sequence of reduction, toluene-*p*-sulphonation, and reduction applied to (**13**) itself, followed by deacetalization, yielded ketone (**15**). Base-catalysed condensation[10] of (**15**) with methyl formate gave (**16**), which reacted with toluene-*p*-sulphonyl azide or the corresponding *p*-nitro compound to form the diazoketone (**17**).[11] Irradiation ($\lambda > 310$ nm) of (**17**) in methanol induced Wolff rearrangement and formation of the two ring-contracted esters, (**18a**) and (**18b**) (*ca.* 1 : 3, 20%). The major isomer could be assigned the stereochemistry of (**18b**) with good precedent,[6,12] since methanol addition to the intermediate ketene should be favoured from the less hindered back side. The structure of (**18b**), which was purified by preparative gas chromatography, is strongly supported by its ^{13}C n.m.r. spectrum and its 300 MHz ^{1}H n.m.r. spectrum; in the latter the chemical shifts and coupling constants could be assigned for the signals of all protons except those associated with the two methylene groups of the five-membered ring. These data are in good accord with those for (**19**)[6] and other derivatives of (**5**).[5,6] The esters (**18**) are sufficiently stable to permit gas chromatography for a half hour at 130 °C with only a few percent decomposition.



(18) a, X = H, Y = CO$_2$Me

b, X = CO$_2$Me, Y = H



(19)

All other new compounds illustrated also have spectroscopic properties fully compatible with the structures assigned. All except the diazoketones (**12**) and (**17**) were further characterized by elementary analysis or high resolution mass spectrometry.

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