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A NEW AND FACILE HYDROAZULENE FORMATION : EVIDENCE FOR THE THERMAL OXYGEN TO OXYGEN MIGRATION OF A TRIMETHYLSILYL GROUP

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SUMMARY

Thermolysis of the 2,5-bis(trimethylsiloxy)-tricyclo[4.4.0.$0^{2,5}$]decan-7-ones 3 and 16 leads to hydroazulenes by a transannular reaction involving a remarkable oxygen to oxygen migration of a silylgroup in the intermediate cyclodecadienones

Recently we have described[2] the photocycloaddition of 1,2-(bistrimethylsilyloxy)-cyclobutene 1, with cyclopentenones and cyclohexenones, leading in the latter case to the tricyclo[4.4.0.$0^{2,5}$]decane system (as in 3 and 16). We have shown that these tricyclic intermediates can be transformed to decalones, upon oxidative cleavage of the 2,5 bond, and hence are suitable for the synthesis of eudesmanes[3]. On the other hand the thermolysis of tricyclo[4.4.0.$0^{2,5}$]decanes is well documented and has been a key step for the synthesis of germacrenes and elemanes[4].

We now report a remarkable oxygen to oxygen migration of a trimethylsilyl group in the intermediate cyclodecadienones[4] obtained upon thermolysis of 3 and 16. This thermal transannular reaction provides an efficient entry into the hydroazulene skeleton.

The thermolysis of 3 (from 1 and (-)-piperitone 2; 75 % yield[2,5]) for 2.5 hr at 215° (1.3 mol solution, benzene, sealed pyrex tube), yielded two major products (>80 % by GC analysis; isomers, CIMS; MH^+ at m/z = 283; for $C_{20}H_{38}O_3Si_2$, M = 282), however their instability did not permit their isolation. If the thermolysis mixture (20 mL) was first hydrolysed with hydrochloric acid (5 N, 10 mL) in 30 mL of ether for 4 hr at room temperature, then separation by preparative HPLC (ethyl acetate-hexane 35:65) afforded, in isolated yields, the hydroazulenes : 9 (21 %); 10 (9 %) and 11 (54 %) together with two isomers of the triketone 12 (10 %). [9; m.p. 121.5°; ^{1}H NMR (360 MHz, $CDCl_3$), δ = 1.29 (s, 3H), 2.64 (d, 13.6 Hz, 1H), 2.83 (dd, 13.60 and 0.76 Hz, 1H); 10; m.p. 114°C; ^{1}H NMR (360 MHz, $CDCl_3$), δ = 1.28 (s, 3H), 2.39 (d, 13.5 Hz, 1H), 2.75 (dd, 13.5 and 1.75, 1H); 11; ^{1}H NMR (360 MHz, $CDCl_3$), δ = 1.27 (s, 3H), 3.06 (dt, 14.20 and 1.65 Hz, 1H) and 3.39 (d, 14.20 Hz, 1H)]. The structure of the hydroazulene 10 was proven by X-ray analysis[6].

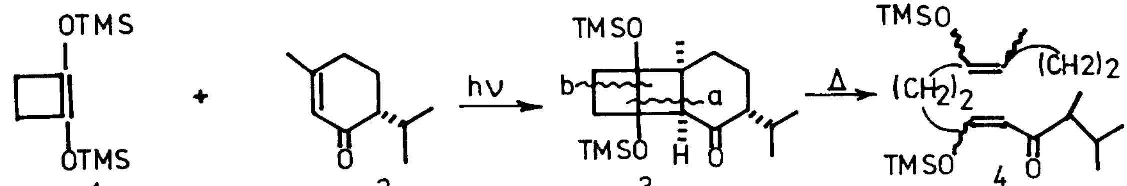
The other isomer was assigned the C-1,C-5 di-epimeric structure 9 on the following grounds. The NMR spectra of 9 and 10 are very analogous; the almost identical δ values for the angular methyl protons (δ = 1.28 and 1.29) suggest that 9 is also a cis hydroazulene[7]. Furthermore the different relative configuration at C-1 and C-4 in isomers 9 and 10 is proven by their respective transformation into two different retro aldol products 13 and 14.

The transannular reaction of the intermediate cyclodecadienone occurs during the thermolysis and not during the hydrolysis, since the cleavage of the trimethylsilyl ethers, in the intermediate, would afford a cyclodecanetrione. The latter would be expected to undergo an internal aldol condensation yielding a bicyclo[5.3.0]dec-1(5)-ene-2,10-dione. The proposed thermal reaction was confirmed by spectral data of the crude thermolysis mixture. The ^{1}H NMR (90 MHz, $CDCl_3$) shows an intense singlet (angular methyl) at δ = 1.1 and a broad singlet for a vinylic proton at δ = 5.6. The IR spectrum reveals the presence of an isolated keto-function ($\bar{\nu}_{C=O}$, 1710 cm^{-1}) and of a double bond ($\bar{\nu}_{C=C}$, 1660 cm^{-1}). These data are consistent with structures such as 5 and 6 but not with the germacrene type intermediate 4.

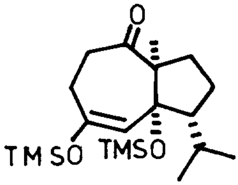
In order to follow the reaction a thermolysis experiment was carried out in boiling undecane (195°) and was monitored by GC-CIMS. Whilst the, now slower, thermolysis conditions afforded again mainly the two major products, a typical analysis after 9 hr revealed six GC peaks (more than 1 %), in a ratio of 1:45:8:15:25:6. Peak 4 is the starting material 3; peak 1 (MH^+ at m/z 293) corresponds to 7. The four other products are isomers (MH^+ at m/z 383). The presence of only one intense signal (for the angular methyl protons (δ = 1.1, vide supra) in the ^{1}H NMR of the crude mixture, indicates identical ring fusions for both major isomers[7], thereby allowing the structural assignment of GC peaks 2 and 5 as 5 and 6. The minor peaks could correspond to 8 (isomers) and/or to trans fused hydroazulenes. As can be seen, product 11 arises mainly from 5 and 6 by elimination during the subsequent hydrolysis.

Thermolysis of 3 performed in benzene solution at 215° in a sealed pyrex tube for 6 hr suppressed the formation of 8 (and consequently of 12). When the subsequent hydrolysis was carried out with 10 N hydrochloric acid only the enone 11 was obtained in 83 % yield.

To explain the observed products the following mechanism is proposed. The thermolytic cleavage (a) of 3 must lead, when assuming a concerted reaction[8], to a cis-trans cyclodecadienone (4' and/or 4") while the divinyl cyclohexanone 8 arises from cleavage (b) or through Cope rearrangement after cleavage (a). It is obvious that the cis-hydroazulenes 5 and 6 can only be formed by a trimethylsilyl group migration in the cis-cis cyclodecadienone 15 on both conformers 15α (→ 5) and 15β (→ 6). The cis,trans isomers 4' or 4" are thus transformed by two successive Cope rearrangements[9] into 15. A rationale for the absence of trans fused hydroazulenes could be that the thermolytic cleavage (a) of 3 leads mainly to the cis-trans cyclodecadienone 4" which, in contrast to 4', cannot give the



1 2 3 4



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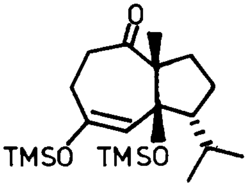

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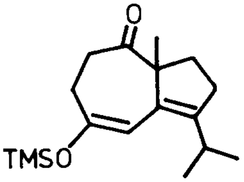

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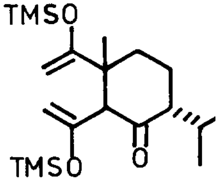

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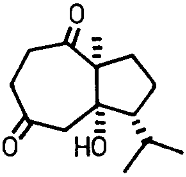

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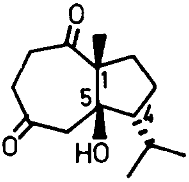

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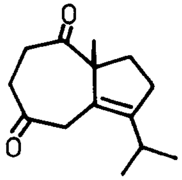

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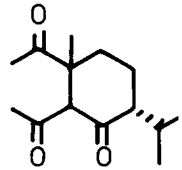

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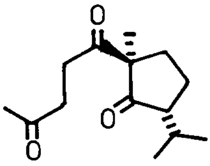

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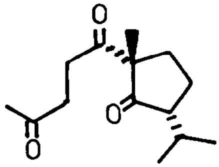

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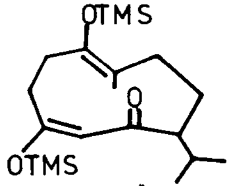
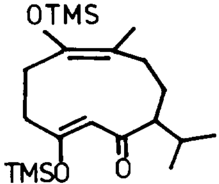
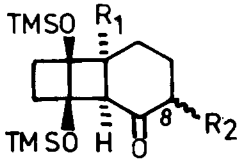


4'



4''



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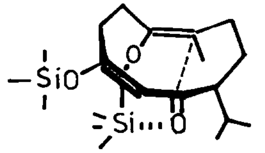
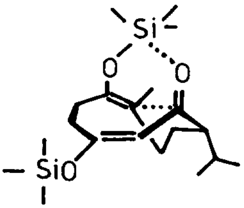
a $R_1 = Me$; $R_2 = H$

b $R_1 = Me$; $R_2 = CH_2COOMe$

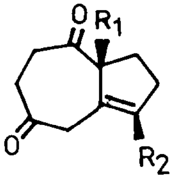
c $R_1 = R_2 = H$



15 α



15 β



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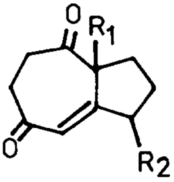

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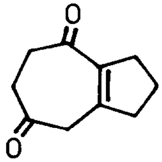

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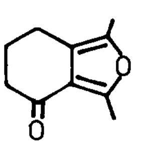

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transannular reaction.

As already mentioned the enone 11 can be obtained as the single product in high yield, which represents a three step formation of a functionalized hydroazulene from (-)-piperitone in 60 % overall yield. In order to test the generality of this transannular migration the photo-adducts 16a, b and c, were subjected to thermolysis (benzene 215°, sealed pyrex tube) for 6 hr and to subsequent hydrolysis with 10 N hydrochloric acid. The adduct 16a led to a mixture of enones 17a (31 %) and to 18a (35 %). In contrast to the stereoselective formation of 3 the adduct 16b represents a 1:1 C-8 epimeric mixture; thermolysis and hydrolysis led to 17b in 44 % yield. The unsubstituted analog 16c led to a mixture of the hydroazulene dione 19 (44 %) and the ketofuran 20 (20 %).

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