Tetrahedron Letters,Vol.26,No.43,pp 5277-5280,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

SYNTHESIS AND REARRANGEMENT OF FUNCTIONALIZED DISPIRO[3.0.3.3]UNDECANES - A NEW ENTRY TO [3.3.3]PROPELLANES [1)]

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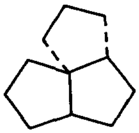
Summary: The functionalized dispiro[3.0.3.3]undecanes 6 and 7 undergo cascade rearrangements to yield the [3.3.3]propellanes 15 and 11, respectively. The formation of 15 proceeds via the bicyclic enone 16.

Naturally occurring sesquiterpenes based on the tricycloundecane skeletons 1, 2 and 3 have been the focus of considerable synthetic interest during the past few years [2)]. Molecular mechanics calculations [3)] predict 1 (ΔH_f^o = -26.7 kcal/mol) and 2 (ΔH_f^o = -25.7 kcal/mol) to be thermodynamically favoured over the vaste majority of their tricycloundecane congeners, but 3 (ΔH_f^o = -29.6 kcal/mol) is predicted to be the most stable of all. It therefore seemed particularly attractive to induce cascade rearrangements in suitable sized dispiranes in order to enter the tricycloundecane energy surface specifically near 1 and to look whether derivatives of 1, 2 and/or 3 would be obtained.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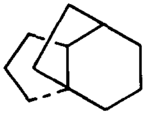
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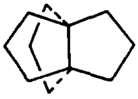
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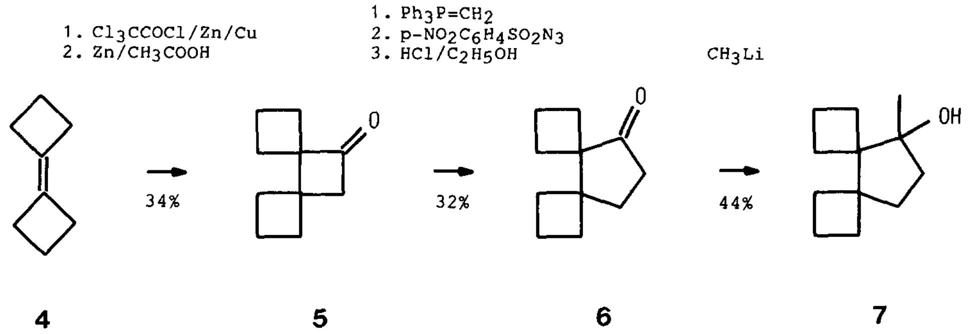
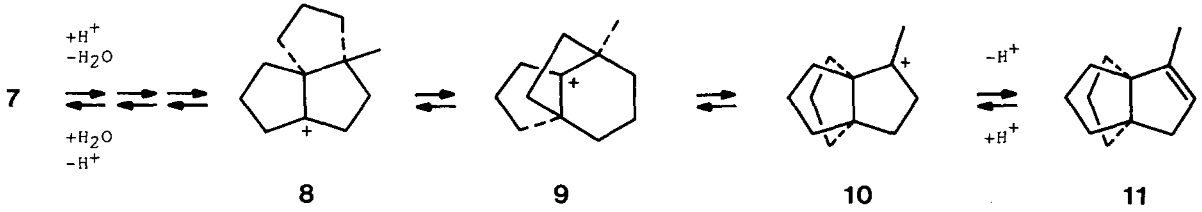
Out of several promising candidates [4)], we chose the dispiranes 6 and 7 as best suited for an initial rearrangement to the skeleton of 1 [5)]. 6 and 7 were obtained as follows: addition of dichloroketene [6)] to bicyclobutylidene 4 [7)] and subsequent dechlorination [6)] of the resulting dichloroketone gave the dispiroketone 5 [8)] which was then homologated to 6 [8)] by a sequence of methylenation, reaction with p-nitrobenzenesulfonic acid azide and hydrolysis of the resulting ring expanded imide [9)]. Addition of methyllithium then yielded 7 [8)], albeit extensive enolization led to the recovery of up to 50% of unchanged 6.

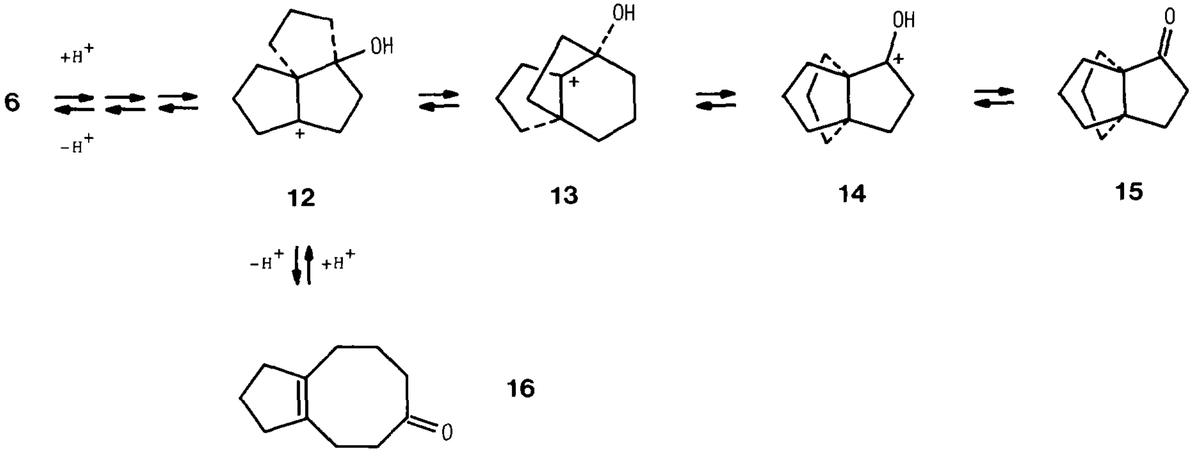
When alcohol 7 was treated with an equimolar amount of a 0.54 molar solution of anhydrous p-toluenesulfonic acid in benzene for 2 h at +70°C, a quantitative conversion to the propellane 11 [8)] was observed. However, treatment of ketone 6 with



an equimolar amount of the same solution for 12 h at +20°C resulted in a quantitative conversion to the bicyclic enone 16 8). The same conversion was complete within 10 min at +70°C, but after 12 h at +70°C, the propellanone 15 10) had formed instead.

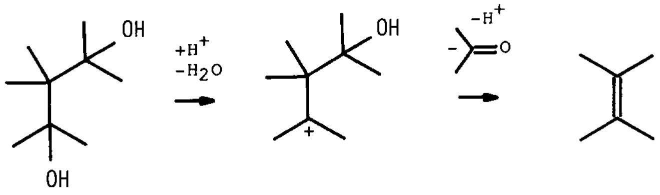
These results may be rationalized as follows: after protonation (6, 7) and dehydration (7) both 6 and 7 undergo the expected 5) twofold cyclobutylmethyl-cyclopentyl rearrangement to yield the tricycloundecyl carbenium ions 8 and 12, respectively. At this stage a rapid but reversible ring opening of the ß-hydroxycarbenium ion





12 to the bicyclic enone 16 occurs, while 8 undergoes two further 1,2-shifts to yield the propellane 11 (8-9-10-11). To account for the final conversion of the bicyclic enone 16 to the propellanone 15 a carbenium ion mediated transannular ring closure to 12[13] followed by two 1,2-shifts (16-12-13-14) may be anticipated. Support comes from the fact that 15 (ΔH_f^o = -54.0 kcal/mol) is predicted[14] to be thermodynamically favoured over both 16 (ΔH_f^o = -40.7 kcal/mol) and 6 (ΔH_f^o = -5.5 kcal/mol).

Finally, the ring opening of 12 leading to the bicyclic enone 16 deserves comment. This opening is an intramolecular variant of the known[15] fragmentation of the 1,3-diol 17 which also proceeds via a ß-hydroxycarbenium ion (18) yielding tetramethylethylene 19 and acetone. The potential value of this fragmentation for the synthesis of other acyclic, mono- and bicyclic enones seems obvious.



17 18 19

In summary, the synthesis and rearrangement of suitable functionalized dispiro[3.0.3.3]undecanes provides a new and efficient entry to tricycloundecanes. Acid catalyzed rearrangements in nonnucleophilic solvents have shown to give derivatives of 3, acid catalyzed rearrangements in nucleophilic solvents and rearrangements induced by thionylchloride in pyridine[5] should lead to derivatives of 1 and/or 2. The synthesis of naturally occurring sesquiterpenes based on the skeletons of 1, 2 and 3 might thus be feasible. Research towards this goal is in progress.

Acknowledgement: Financial support of the Fonds der Chemischen Industrie is gratefully acknowledged.

References and notes

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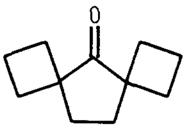
2) Reviews: L.A.Paquette, Top. Curr. Chem. 79, 41 (1979) and 119, 1 (1984); M.Vandewalle and P. de Clercq, Tetrahedron 41, 1767 (1985).

3) E.Ōsawa, K.Aigami, N.Takaishi, Y.Inamoto, Y.Fujikura, Z.Majerski, P.von R. Schleyer, E.M.Engler and M.Farcasiu, J. Am. Chem. Soc. 99, 5361 (1977).

4) Other candidates for an initial rearrangement to the skeleton of 1 are 20 and 21 while 22 and 23 are suited for an initial rearrangement to the skeleton of 2. None of these systems has yet been described.



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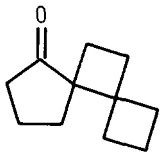

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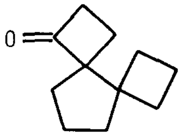

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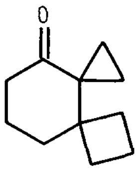

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5) The exceptional ease of the ring enlargement of spiroannulated four-membered rings leading to edge-annulated five-membered rings has recently been demonstrated: L.Fitjer, M.Giersig, W.Clegg, N.Schormann and G.M.Sheldrick, Tetrahedron Lett. 1983, 5351.

6) These reactions have been performed as described for the synthesis of 2,2,-3,3-teramethylcyclobutanone: D.A.Bak and W.T.Brady, J. Org. Chem. 44, 101 (1979).

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8) All new compounds gave correct elemental analyses and/or high resolution mass spectral data. IR, ^{1}H NMR, ^{13}C NMR and mass spectral data are in accord with the structures given. ^{13}C NMR data (20 MHz, CDCl$_3$, unless otherwise stated): 5: 15.68, 16.16, 26.00, 29.21, 39.51, 55.93, 66.92, 212.65; 6: 14.33, 14.94, 23.90, 26.46, 30.58, 33.66, 47.89, 56.77, 219.82; 7: 15.02, 15.96, 21.53, 24.16 (multiplet selection revealed the coincidence of a primary and a secondary carbon atom), 29.90, 31.09, 34.44, 36.83, 51.20, 55.87, 81.93; 11: 13.82, 25.98, 37.75, 41.85, 47.48, 60.30, 70.17, 122.12, 144.07; 16 (C$_6$D$_6$): 22.26, 23.17, 24.75, 28.24, 36.12, 37.28, 40.43, 45.85, 136.51, 137.21, 211.50.

9) For other examples of this useful homologation sequence see: R.A.Wohl, J. Org. Chem. 38, 3862 (1973); S.P.Mc Manus, M.Ortiz and R.A.Abramovitch, ibid. 46, 336 (1981); L.Fitjer, Chem. Ber. 115, 1047 (1982).

10) The propellanone 15 has formerly been obtained by acid catalyzed rearrangement of the tricycloundecanes 24 11) and 25 12). IR, ^{1}H NMR and mass spectral data were in accord with the data given in ref. 12). The ^{13}C NMR data have not yet been reported and are as follows: 15 (C$_6$D$_6$): 26.49, 31.62, 37.38, 37.68, 41.00, 58.89, 65.97, 220.10.

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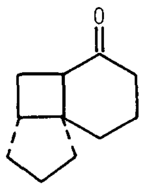

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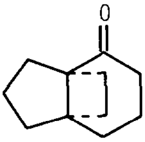

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13) A carbenium ion mediated transannular ring closure of a functionalized bicyclo[6.3.0]undecane has recently been described: G.Mehta and K.S.Rao, Tetrahedron Lett. 1984, 3481.

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(Received in Germany 22 July 1985)