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TOWARDS [6.5]CORONANE - FIVEFOLD CYCLOBUTYLMETHYL-CYCLOPENTYL REARRANGEMENT IN A PENTASPIROHENEICOSANOL[1)]

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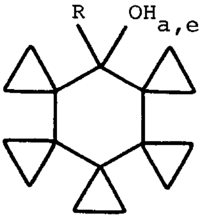
Summary: The synthesis and successful rearrangement of the pentaspirane 4 yields the hexacyclic 11, whose stereochemistry was unequivocally established as all-cis by X-ray analysis of a single epoxide 12 derived therefrom. A synthesis of [6.5]coronane 5 thus seems feasible.

A potentially useful technique for the construction of repeating partial structures, and hence for the synthesis of [m.n]coronanes[2)], is cascade rearrangement. After promising precursors of [6.4]coronane 3 have been obtained[2)] via the successful rearrangement of the pentaspiranes 1 (R=H,CH_3) to 2 (R=H,CH_3), we herein report on the synthesis and rearrangement of the homologous 4 as a potential precursor of [6.5]coronane 5.



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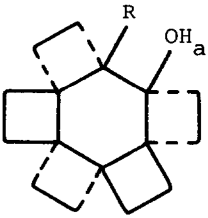

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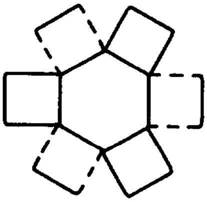

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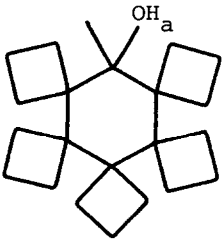

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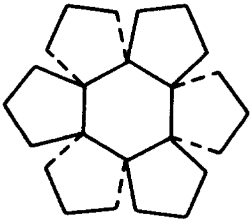

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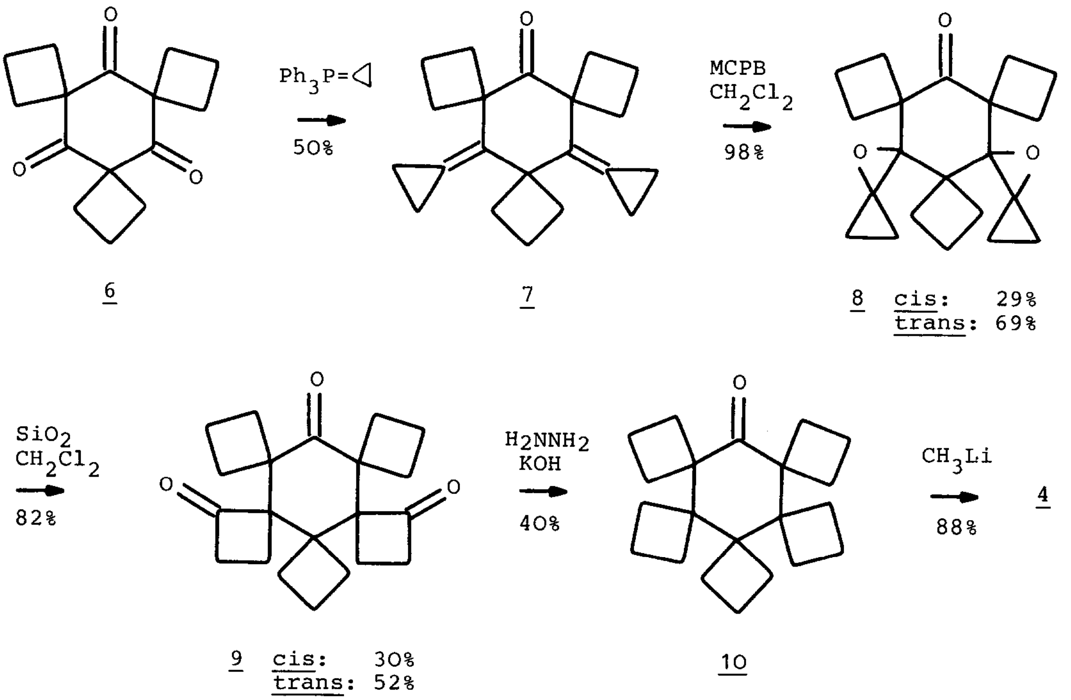
The pentaspirane 4 was obtained as follows: trimethyleneketene trimer 6 3) was reacted with cyclopropylidenetriphenylphosphorane in benzene (6 equiv., 20 hr, 70°C) to give 50% of the diene 7 (mp 70°C) 4) which was then treated with m-chloroperoxybenzoic acid in methylene chloride (2.5 equiv., 8 hr, rt) to provide 98% of a 3:7 mixture of cis-8 4,5) and trans-8 4,5) as colourless oil. Oxaspiropentane-cyclobutanone rearrangement of this mixture was accomplished by chromatography over silica gel in methylene chloride and gave 30% cis-9 (mp 177-178°C) 4,5) and 52% trans-9 (mp 180-181°C) 4,5). Trans-9 was selectively reduced by sequential treatment with hydrazine hydrate in triethyleneglycol (8 equiv., 3.5 hr, 140°C) and potassium hydroxide (6 equiv., 2.5 hr, 180°C) to give 40% of the monoketone 10 (mp 137-138°C) 4), which was ultimately transformed to the desired 4 (mp 214-216°C, 88% yield) 4) by treatment with methyllithium (5 equiv., 15 min, rt) in ether. As indicated by ^{1}H NMR 6), the methyl group of 4 adopts an equatorial position.



6

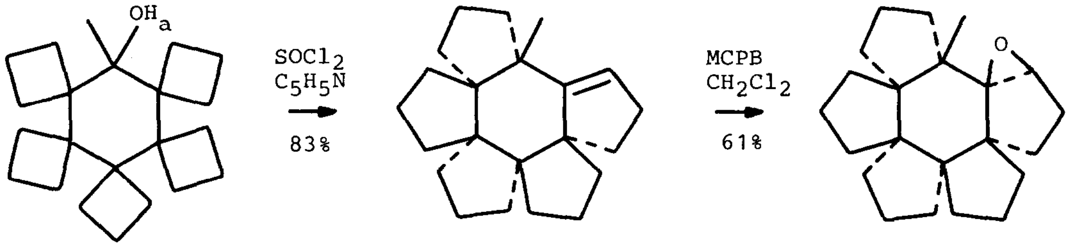
7

8 cis: 29%
trans: 69%

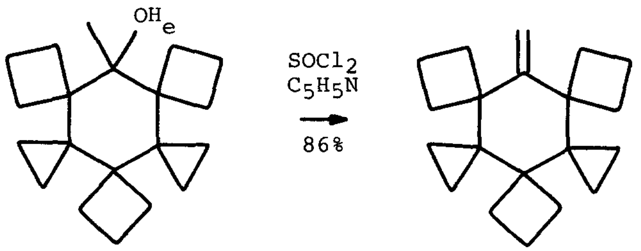
9 cis: 30%
trans: 52%

10

Surprisingly, cascade rearrangement was initiated and complete within 15 min at 0°C by treatment of 4 with thionylchloride (5 equiv.) in pyridine. No exocyclic olefin could be detected, the hexacyclic 11 (mp 227-247°C, 83% yield) 4) was isolated instead. Structure and stereochemistry of 11 were unequivocally established by X-ray analysis 8) of a single epoxide 12 (mp 234-236°C, 61% yield) 4) derived from 11 by treatment with m-chloroperoxybenzoic acid in methylene chloride (1.8 equiv., 3 hr, rt). Both 11 and 12 (figure 1) show all-cis configuration and contain the methyl group in an axial position. It is thus obvious,that 12 must have been formed from 11 by equatorial attack of the reagent.



4 11 12



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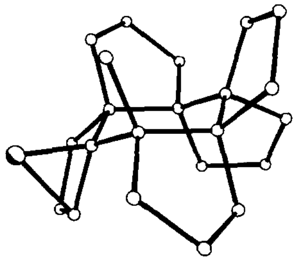

Figure 1. Molecular structure of 12

To account for the unusual behaviour of 4 towards thionylchloride in pyridine, a simultaneous fivefold cyclobutylmethyl-cyclopentyl rearrangement, caused by the perfect antiperiplanar array of all bonds to be broken and formed, may be anticipated. Support comes from the fact, that inversion of configuration at the oxygen-bearing carbon atom, as realized in 13[6,7], completely prevents any rearrangement. Faced with a now synclinal orientation of the hydroxyl group with respect to all neighboring spirocyclobutane bonds, thionylchloride here causes elimination and yields the corresponding exocyclic olefin 14[7] exclusively.

In summary, cascade rearrangement is not restricted to polyspiranes of three-membered rings. As the substituent of 4 may be changed without inverting the configuration, a synthesis of [6.5]coronane 5 seems feasible.

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References and Notes

Dedicated to Professor Hans Brockmann on the occasion of his eightieth birthday.

1) Polyspiranes, 8, Cascade Rearrangements, 3; for communications 7 and 2 see ref. 2b). Presented in part at the 29th IUPAC Congress in Cologne, Germany, 5-10 June 1983.

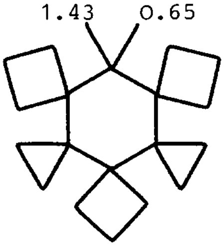
2) a) L.Fitjer and D.Wehle, Angew. Chem., Int. Ed. Engl. 18, 868 (1979); b) L.Fitjer, D.Wehle, M.Noltemeyer, E.Egert and G.M.Sheldrick, Chem. Ber. 116 (1983), in press.

3) J.L.E.Erickson, F.E.Collins and B.L.Owens, J. Org. Chem. 31, 480 (1966).

4) Cis- and trans-8 were characterized by ^{13}C NMR only; correct elemental analyses, IR, ^{1}H NMR, ^{13}C NMR and mass spectral data were obtained in all other cases. ^{13}C NMR data (50.3 MHz) are as follows: 4 ($CDCl_3$): 16.61, 21.05, 24.76, 25.99, 26.83, 27.09, 27.96, 28.28, 48.68, 49.39, 50.84, 79.96; cis-8 (C_6D_6): 2.11, 2.60, 16.91, 17.34, 25.27, 26.00, 27.63, 29.52, 46.04, 55.11, 59.37, 67.86, 208.53; trans-8 (C_6D_6): 2.18, 2.57, 16.66, 17.44, 26.09, 27.50, 27.81, 46.04, 54.35, 59.14, 67.79, 209.41; cis-9 (C_6D_6): 13.95, 15.76, 16.60, 24.59, 26.31, 28.27, 30.49, 44.27, 45.49, 53.59, 76.96, 207.06, 210.93; trans-9 ($CDCl_3$): 15.60, 16.68, 17.53, 26.96, 28.42, 29.44, 44.15, 44.96, 53.01, 78.28, 208.04, 212.25; 10 (C_6D_6, 70°C): 16.36, 16.40, 17.06, 25.61, 26.25, 28.79, 48.82, 52.08, 58.57, 211.44; 11 ($CDCl_3$): 21.10, 21.25, 21.40, 23.72, 28.92, 29.30, 36.95, 37.77, 37.84, 38.87, 39.06, 39.62, 39.72, 40.48, 44.96, 56.91, 57.22, 58.23, 58.47, 121.50, 156.00; 12 ($CDCl_3$): 20.50, 20.59, 21.17, 22.38, 22.67, 27.07, 35.11, 36.91, 37.89, 38.01, 38.60, 38.80, 39.23, 39.70 (two lines, not resolved), 45.05, 54.54, 57.41, 58.46, 59.13, 66.03, 71.57.

5) Owing to their different symmetry, both cis/trans-8 and cis/trans-9 can most easily be distinguished by means of ^{13}C NMR.

6) The assignment is based on a ^{1}H NMR chemical shift correlation with 15[7] and 1, $R=CH_3$[2] as model systems which both exist in a fixed chair conformation.



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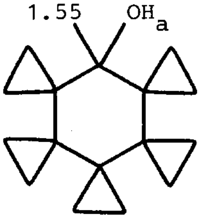
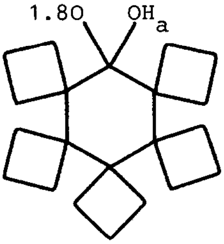


1, $R=CH_3$



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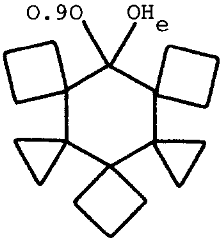

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7) The synthesis and reactions of 13 and 15 will be published elsewhere.

8) 12 forms triclinic crystals, a = 7.228(1), b = 8.537(3), c = 8.610(3) Å, α = 115.00(3), β = 106.07(2), γ = 102.85(2)°, Z = 1, space group $P\bar{1}$. The structure was solved from 1195 diffractometer reflections with $F>4\sigma(F)$ and refined with anisotropic thermal parameter and constrained H atoms to R = 0.08. The molecule lies two-fold disordered on a centre of symmetry. Full details will be published elsewhere.

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