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A NEW PATH TO THE TRICYCLO[5.4.0.0^{2,8}]UNDECANE SKELETON.

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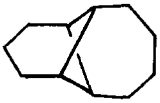
Summary: Starting from 7-methoxybenzosuberone the tricyclo[5.4.0.0^{2,8}] undecane ring system is obtained by a highly regio- and stereoselective ring closure.

The easy access to the tricyclo[5.4.0.0^{2,8}]undecane system (1) is of considerable interest for several reasons: 1) π-systems derived from 1 ($C_{11}H_{11}$) are of interest with regard to the question of conjugation between two



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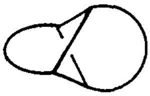

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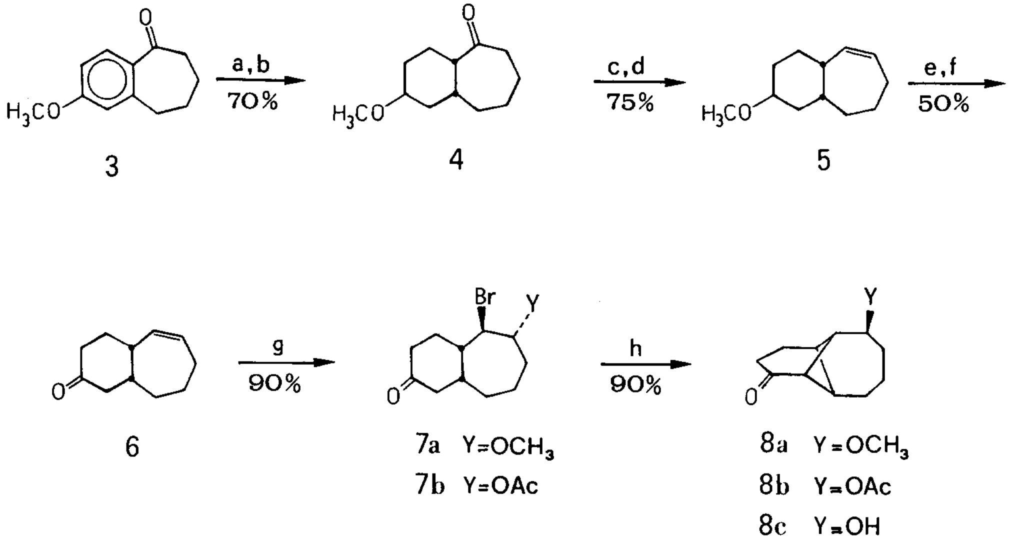
perpendicular π-systems separated by a four membered ring[1], and 2) 1 represents the skeleton of longipinene and its derivatives[2] and is so far only accessible in a light-induced ring closure of cyclodeca-1,5-diene derivatives[2b] and subsequent ring enlargement. In our efforts to synthesize tricyclo alkanes and alkenes of type 2[3] we found a relatively simple and general route to the skeleton of 1. Our approach to 1 is summarized in Scheme 1. From the readily available 7-methoxybenzosuberone (3)[4] the bicyclic ring systems 4-6 can be obtained in good yields using known procedures[5]. The pivot point of the synthesis is the highly stereo- and regioselective formation of 7 when 6 is treated with NBS and a nucleophile (e.g. methanol or Na-acetate).

Subsequent treatment of 7 with a strong base[6] produces 8, a tricyclo[5.4.0.0^{2,8}]undecane derivative functionalized in both bridges.



Scheme 1. Synthesis of 8 a) Ru on Al_2O_3,5%, H_2, 100 atm, 80°C; b) Al-isopropoxide, acetone, toluene, 48 h, 90°C;c) pCH_3-C_6H_4-SO_2NHNH_2 in EtOH, 3h reflux, 12 h r.t.; d) THF, BuLi, 0-5°C; e) Me_3SiCl, NaI, pyridine in CH_3CN, r.t. 14 h; f) DMSO, $(COCl)_2$ in CH_2Cl_2, NEt_3 -60°C; g) 7a: NBS in CH_3OH, r.t. 24 h; 7b: NBS, NaOAc, Ac_2O in CH_3COOH, 24 h r.t.; h) NaH in DMSO, 1 h, 70°C.

The structural assignments of 3-8 are based on their spectroscopic data. The most important data of the key-compounds are listed in Table 1.

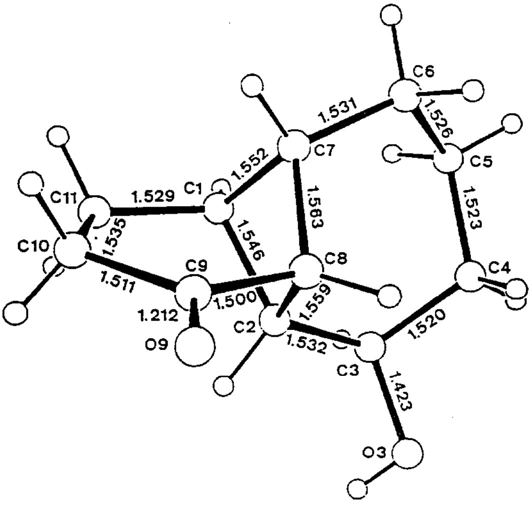
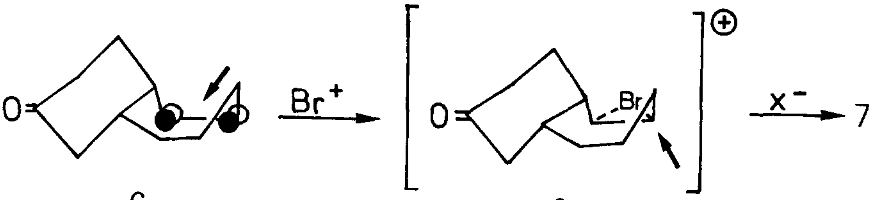


Figure 1. Bond lengths of 8c as determined by X-ray structure analysis[7]. Standard deviations 0.002 – 0.003 Å.

The stereochemistry of 8 has been determined by an X-ray study of 8c(Y=OH). The bond lengths of 8c are shown in Fig. 1[7]. The configuration on C(3) of 8c is R and the spiro system has M configuration or vice versa for the enantiomer.
The high degree of regio- and stereoselectivity exhibited during the formation of 6 is ascribed to the conformation of 6. Molecular models and force field calculations on 6 suggest that conformation 6a represents a local energy minimum. The attack of an electrophile (e.g. Br^+) at the double bond takes place preferentially from the exo-side for steric reasons, as indicated by an arrow in 6a. The second step, the attack of 9 by a nucleophile must occur from the endo-side, again for steric reasons, at the position α to the CH_2 group.



6a 9

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Table 1. Selected Spectroscopic Data of 7a and 8a.

7a ^{1}H-NMR (90MHz, $CDCl_3$, TMS) δ: 4.35 (1H,m); 3.4 (3H,s); 2.9-1.4 (14H,m); ^{13}C-NMR (20.0 MHz), $CDCl_3$, TMS) δ: 210.37(s); 85.15 (d); 60.07 (d); 57.20 (q); 48.62 (t); 46.90 (d); 40.52 (t); 36.37 (d); 30.16 (t); 29.24 (t); 28.88 (t); 20.91 t); IR(film): 2920(vs); 2820(s); 1705(vs,C=O); 1050(vs, OCH_3) cm^{-1}.

8a ^{1}H-NMR (300 MHz, $CDCl_3$, TMS) δ: 3.56 (1H,m); 3.29(3H,s); 2.88(1H,d); 2.62 (2H,m); 2.39 (1H,t); 2.29 (1H,m); 2.21 (1H,m); 2.1-2.0 (2H,m); 1.95-1.7 (6H,m); ^{13}C-NMR (75.46 MHz, $CDCl_3$, TMS) δ: 212.5(s); 79.1(d); 55.6(q); 51.05(d); 43.9 (d); 41.7(d); 36.8(d); 31.8(t); 30.0 (t); 29.3(t); 25.2(t); 19.4(t); IR(film): 2920 (s), 1710 (s,C=O); 1080(s,OCH_3) cm^{-1}.

REFERENCES

[1] P. Bischof, R. Gleiter, R. Haider, **J. Am. Chem. Soc.** 100, 1036 (1978).

[2]a] L.V. Roman, R.E. del Rio, J.D. Hernandez, C.M. Cerda, D. Cervantes, R. Cataneda, P. Joseph-Nathan, **J. Org. Chem.** 50, 3965 (1985); F. Bohlmann, L.N. Dutta, W. Dorner, R.M. King, H. Robinson, Phytochem. 18, 673 (1979); I. Ognyanov, M. Todorova, V. Dimitrov, J. Ladd, H. Irngartinger E. Kurda, H. Rodewald, **Phytochem.** 22, 1775 (1983); b) M. Miyashita, A. Yoshikoski, **J.Am.Chem.Soc.** 96, 1997 (1974).

[3] R. Gleiter, W. Sander, H. Irngartinger, A. Lenz, **Tetrahedron Lett.** 23, 2647 (1982); R. Gleiter, H. Zimmermann, W. Sander **Angew. Chem.** 98, 893 (1986); **Angew. Chem. Int. Ed. Engl.**, 26, 906 (1986); R. Gleiter, W. Sander, I. Butler-Ransohoff, **Helv. Chim. Acta** 69, 1872 (1986).

[4] M.G. Hicks, G. Jones, H. Seickh, **J. Chem. Soc. Perkin Trans. I**, 1984, 2297.

[5]a] D. Ginsburg, W.J. Rosenfelder, **Tetrahedron** 1, 3 (1957); C. Djerassi, **Org. React.** 6, 207 (1951); b) R.H. Shapiro **Org. React.** 23, 405 (1976); c) K. Omura, D. Swern, **Tetrahedron** 34, 1651 (1978); d) G.A. Olah, S.C. Narrang, G.B. Gupta, R.Malhotra, **J. Org. Chem.** 44,1247 (1979).

[6] C.H. Heathcock, R.A. Badger, J.W. Patterson Jr., **J. Am. Chem. Soc.** 89, 4133 (1967).

[7] Crystallographic data of 8c: a= 11.799(2), b= 7.832(2), c=10.047(2)A; Pca2_1; Z=4; D_c= 1.29 g/cm^3; 1181 independent reflections, 1053 observed reflections [I>2.5 σ(I)]; R=0.032. Complete structural data have been submitted to the **Cambridge Crystallographic Data Centre**.

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