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THE SYNTHESIS OF 2,6-DIMETHYLENETRICYCLO[3.3.0.0^{3,7}]OCTANE**

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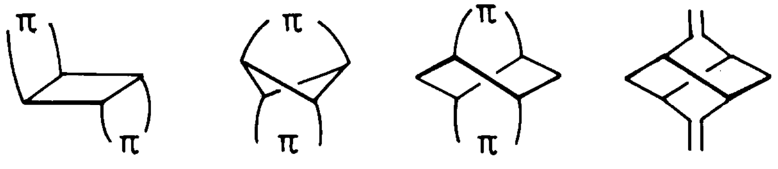
The synthesis of the title compound is reported together with that of 2-methyl-6-methylenetricyclo[3.3.0.0^{3,7}]octane. During the synthesis a rearrangement of the tricyclo[3.3.0.0^{3,7}]octane skeleton to the tricyclo[3.2.1.0^{3,6}]octane system has been observed.

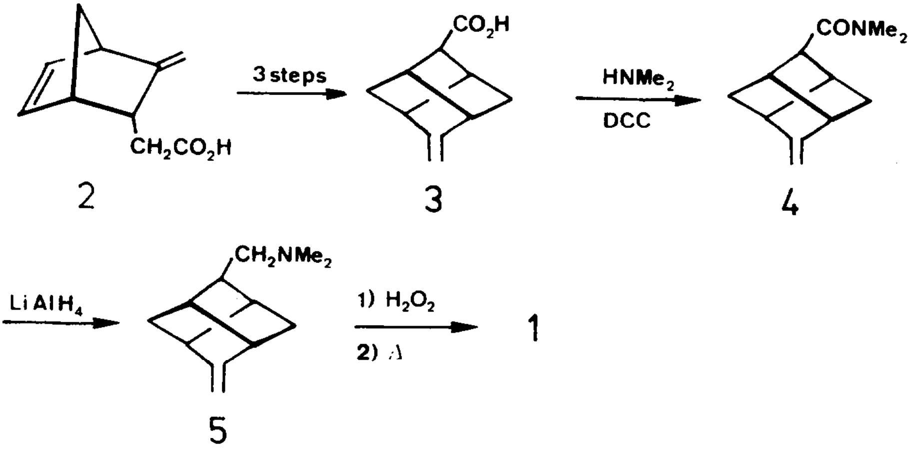
Our recent studies revealed that a four membered ring could very well act as a relay between two π-systems[1] if they are connected as shown in A or B. In relation to these investigations we are interested to study the interaction



A B C 1

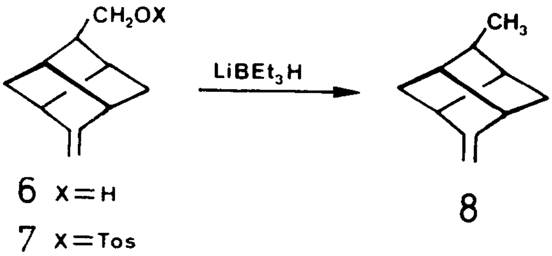
of two π fragments via a six membered ring as shown in C. One of our target molecules is 2,6-dimethylenetricyclo[3.3.0.0^{3,7}]octane (1), an isomer of twistadiene.

To synthesize 1 we followed a procedure used by Nakazaki et al.[2] for the synthesis of coaxially substituted tricyclo[3.3.0.0^{3,7}]octane derivatives. The key intermediate, the acid 3, is obtained in a very moderate overall yield of about 10% from the acid 2 involving an intramolecular ketene addition originally developed by Sauers et al[3].



To synthesize 1 we converted 3 into the tertiary amine 5 via the amide 4. Pyrolysis of the N-oxide at 150°C/2mm yielded the diene 1 (10% yield after purification by prep. GLC)[5]. Due to the high symmetry of the species (D_2), its ^{1}H NMR spectrum exhibits only three signals at δ = 4.38(4H,s), 2.54 (4H,br.s) and 1.48(4H,br.s).

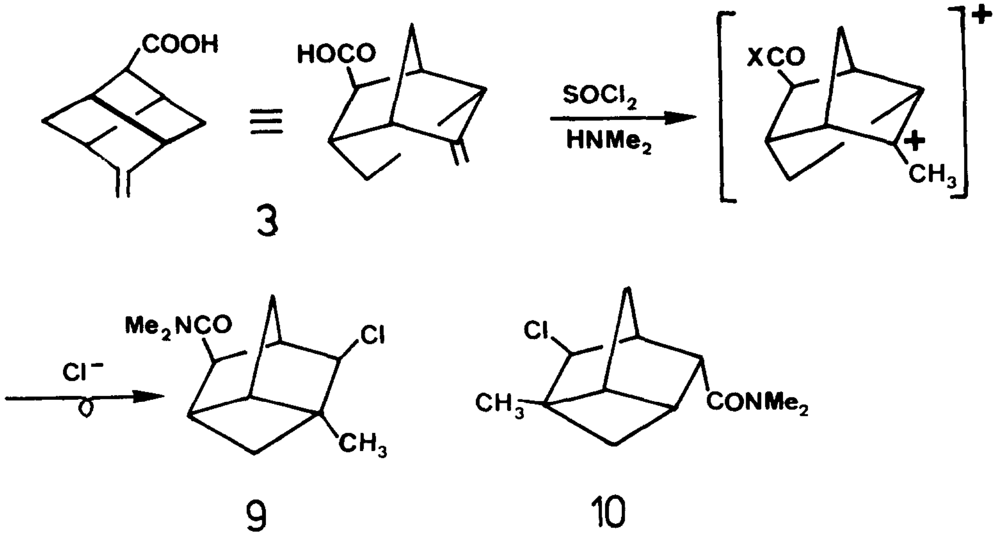
Reduction of 3 with $LiAlH_4$ provided the alcohol 6 in 70% yield. The tosylate (7) was treated with superhydride to yield the hydrocarbon 8 (45%). All



attempts to obtain 1 from 7 by elimination reactions failed.

When we treated 3 with $SOCl_2$ and dimethylamine in order to obtain 4 a mixture of three compounds was found in ratios of 57:38:5. After separation by means of MPLC the structure of the major products could be identified as the tricyclo[3.2.1.0^{3,6}]octane derivatives 9 and 10. The minor product proved to be

4. The structures of 9 and 10 were determined by X-ray analysis[4]. Their generation can be rationalized by a rearrangement of the tricyclo[3.3.0.0^{3,7}]octane system to the tricyclo[3.2.1.0^{3,6}]octane skeleton after protonation[5].



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References and Notes

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[3] R.R. Sauers, K.W. Kelly, B.R. Sickles, J. Org. Chem. 37, 537 (1972) and references therein.

[4] We are indepted to H. Irngartinger, H. Rodewald and U. Huber-Patz for the X-ray analysis of 9 and 10. The results will be reported in the full paper.

[5] All compounds have been characterized by elemental analysis as well as by their ^{1}H, ^{13}C NMR, IR and mass spectra. Selected data:
1: ^{13}C(75 MHz, $CDCl_3$/TMS)δ: 163.0, 92.6, 44.4, 42.0; GLC-FTIR($\tilde{\nu}$[cm^{-1}]): 3078 (w,CH), 3004 (vs), 2970 (vs), 1697 (w,C=C).
8: ^{1}H NMR(300 MHz, $CDCl_3$, TMS)δ: 4.17(s,2H), 2.47(m,1H), 2.40(m,1H), 2.08-2.02(m,2H), 2.01(dd, J_1= 10.7,J_2= 2.6,1H), 1.90(t br., 1H), 1.58 (dd, J_1= 9.7), J_2= 2.6, 1H), 1.29(dd, J_1= 9.6, J_2= 2.6, 1H), 1.26 (td, J_1= 10.2, J_2= 2.6, 1H), 0.91(d,J= 7.0, 3H), ^{13}C NMR(75 MHz, $CDCl_3$/TMS)δ: 165.2(s), 89.2(t), 47,7(d), 44.9(t), 44.0(d), 41.8(d), 41.4(d), 39.5(d), 39.4(d), 15.4(q).
9: mp.107-108^{o}C, ^{1}H NMR(300MHz,$CDCl_3$/TMS)δ: 4.05 (s, 1H), 3.08 (s, 3H), 2.92 (s, 3H), 2.84 (s, 1H), 2.66 (s, 1H), 2.59-2.50 (m, 2H), 2.19 (dd, J_1= 10.6, J_2= 6.6, 1H), 2.04 (dd, J=11,5 1H), 1.80 (dd, J_1= 11.7, J_2= 1.3, 1H), 1.47 (d,J= 10.6, 1H), 1.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$/TMS)δ: 172.4 (s), 71.8 (d), 51.2 (d), 51.0 (d), 46.6 (s), 46.5 (d), 40.7 (t), 37.3 (q), 35.6 (q), 34.5 (d+t), 21.6 (q).
10: mp.107-108^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$/TMS)δ: 5.12 (s, 1H), 2.96(s,3H), 2.93 (s, 3H), 2.91 (s br., 2H), 2.62 (m, 1H), 2.48 (dd, J_1= 11.5, J_2=6.6, 1H), 2.16 (d, J=11.5, 1H), 2.01 (dd, J_1= 10.6, J_2= 6.9, 1H), 1.58 (d, J= 11.0, 1H), 1.33 (d, J= 11.5, 1H), 1.15 (s, 3H), ^{13}C NMR (75 MHz,$CDCl_3$/TMS)δ: 172.5 (s), 70.0 (d), 50.5 (d), 49.1 (d), 48.5 (d), 46.2 (d), 37.5 (t), 36.8 (q), 35.6 (t), 35.4 (q), 31.6 (d), 22.0 (q).

** Dedicated to Professor Wolfgang Lüttke on the occasion of his 65. birthday.

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