

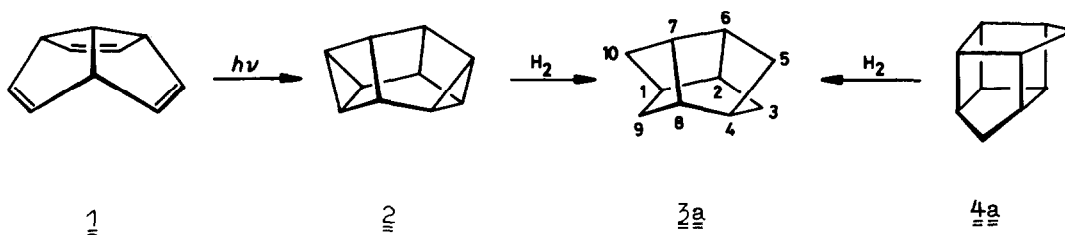
A SIMPLE ROUTE TO HEXACYCLO[4.4.0.0^{2,4}.0^{3,10}.0^{5,8}.0^{7,9}]DECANE ("BARETTANE")
AND PENTACYCLO[5.2.1.0^{2,6}.0^{3,5}.0^{4,8}]DECANE ("DIHYDROBARETTANE")^[**]

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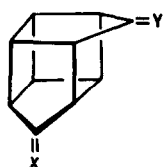
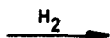
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Our continuing interest^[1] in the photochemical, thermal and metal catalysed rearrangements of (CH)₁₀ hydrocarbons^[2] has led us to look for a new and efficient route to barettane (2). Originally this hydrocarbon was obtained in 7% yield by photolysis of triquinacene (1)^[3], which in turn had to be prepared in a six step synthesis with 10% overall yield from Thiele's acid^[4]. We now report a synthetic sequence leading to barettane (2) in only four steps.



The catalytic hydrogenation of barettane (2) to tetracyclo[5.2.1.0^{2,6}.0^{4,8}]decane ("bisnorditwistane") (3a)^[3] intuitively demonstrates the close relationship between these two carbon skeletons. With a suitable derivative of 3 it should therefore be possible to bring about C-C-bond formation between C-3/C-5 and C-9/C-10. Since the skeleton of 3a is easily accessible by catalytic hydrogenation of the bishomocubane 4a^[5,6] and bishomocubane derivatives^[6], we attempted to prepare suitable bifunctional derivatives of 3 by hydrogenation of the corresponding bishomocubanes (4).

At atmospheric pressure the easily available bishomocubane-6,10-dione mono-ethyleneketal (4b)^[7] took up hydrogen very slowly (10% Pd/C in AcOH), the reaction was incomplete even after a week. With the use of Adam's catalyst, hydrogenation of the strained C-C-σ-bond in 4b was accompanied by reduction of the carbonyl group, but the ketal function remained unchanged even in glacial acetic acid. In methanol with 10% Pd/C at atmospheric pressure 4b was first transformed to the bis-dimethylketal (4c) and then slow hydrogenation to 3c occurred. At higher pressure (40 bar) reduction of the carbonyl group in 4b to a secondary alcohol was the primary reaction. Because of these findings both carbonyl functions in 4e were protected by ketalization with methanol or ethylene glycol. Hydrogenation of the bis-dimethylketal 4c in methanol or the bis-ethyleneketal 4d^[8] in ethanol over 10 % palladium on charcoal at 120 bar produced the tetracyclo[5.2.1.0^{2,6}.0^{4,8}]decane-5,10-dione bis-dimethylketal (3c)^[9] or the bis-ethyleneketal 3d (m.p. 87°C)^[9] in quantitative yield.

43a) X = Y = H₂

b) X = O, Y =

c) X = Y = (OCH₃)₂

d) X = Y =

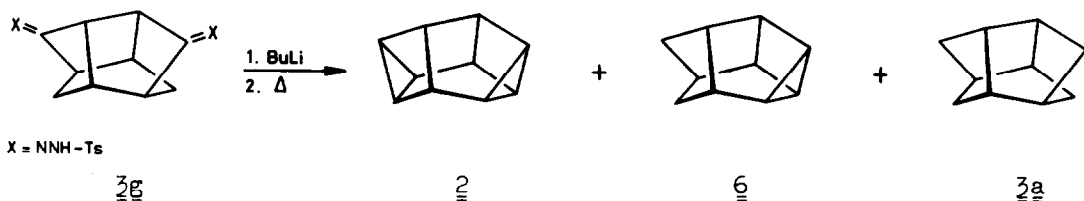
e) X = Y = O

f) X = H₂, Y = O

Deketalization of 3c was achieved in 76% yield by exposure to a mixture of 10% sulfuric acid and tetrahydrofuran (5:2) for 12 h at room temperature. Recrystallization of the crude product from n-hexane yielded pure tetracyclo[5.2.1.0^{2,6}.0^{4,8}]decane-5,10-dione (3e)^[9] as white needles [m.p. 189°C, ¹H-NMR (100 MHz, CDCl₃): τ = 7.49(m, 6(7)-H); 7.77(m, 1(2,3,8)-H); 8.07 (AB system 3(9)-H)].

The ketals 3c and 3d as well as the diketone 3e could be transformed to the bis-tosylhydrazone 3g^[9] (m.p. 142°C). A solution of 3g in dry tetrahydro-

furane was treated with two equivalents of a 15% n-butyllithium solution in n-hexane at 0°C. After evaporation of the solvent the resulting dilithium salt was pyrolyzed at 180°C/0.1Torr and a 17% yield of C₁₀ hydrocarbons was obtained. Vapor phase chromatography indicated three components in a ratio of 5:15:80. The main component proved to be the expected double carbene insertion product barettane (2). It was identical with the photoisomerisation product^[3] of 1 as shown by its vpc retention time, melting point and ¹H-NMR spectrum. After vpc purification the two other compounds were identified by their



¹H-NMR spectra as the pentacyclo[5.2.1.0^{2,6}.0^{3,5}.0^{4,8}]decane (dihydrobarettane) (6)^[9] [rel. yield 15%, ¹H-NMR (100 MHz, CCl₄): τ = 7.44(m, 8-H); 7.63 (bs, 1(2,6)-H); 8.14 (m, 7-H); 8.26 (dd, 3(5)-H); 8.65 (AB system, 10-H); 8.82 (m, 4(9)-H)] and the tetracyclodecane 3a^[5,6] [rel. yield 5%]. 6 and 3a apparently arose from the carbene intermediates abstracting hydrogen from solvent molecules, the last traces of which were difficult to remove from the dilithium salt. 6 was prepared independently in 28% yield by pyrolysis (170°C) of the lithium salt obtained from the tosylhydrazone (m.p. 152°C) of tetracyclo[5.2.1.0^{2,6}.0^{4,8}]decane-5-one (3f)^[10].

Taking into account, that in this synthetic approach barettane 2 is formed by two consecutive carbene insertion steps, each leading to a highly strained bicyclo[2.1.0]pentane unit, the rather low yield (8% isolated) is not too surprising. In spite of this, the new synthesis of 2 is far superior to the photochemical generation from 1^[3], because it can more easily be scaled-up, the separation of the final product mixture is easier and the total yield

over four steps is better. Thus 2 is now available in preparative quantities for a more thorough investigation of its physical and chemical properties.

References and Footnotes

- [*] Author to whom correspondence should be addressed.
- [**] This work was supported by the Deutsche Forschungsgemeinschaft (Project Me 405/9) and the Fonds der Chemischen Industrie.
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