171. Tricyclo[4.2.2.2^{2,5}]dodecane and Tricyclo[4.2.2.1^{2,5}]undecane

Preliminary communication

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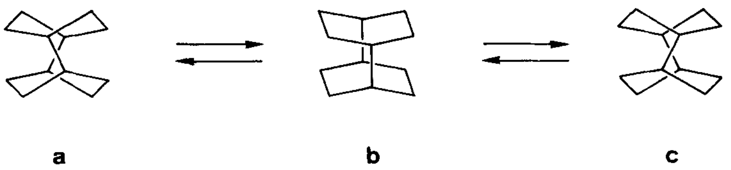
Summary

A synthesis of tricyclo[4.2.2.2^{2,5}]dodecane (**19**), a novel tricyclic $C_{12}H_{20}$ compound, is described. The key intermediate ketone **13** was prepared either from the C_{10}-photodimer **1** of cyclopentadienone or the C_{11}-cycloaddition products **11** and **12**. **13** was also transformed to tricyclo[4.2.2.1^{2,5}]undecane (**8**).

The carbon skeleton of tricyclo[4.2.2.2^{2,5}]dodecane (**19**) consisting of two cyclohexanes connected to each other in the 1 and 4 positions can be represented by the formula **b** *(Scheme 1)*. However, as the boat form of cyclohexane is a flexible conformer, **b** (D_{2h} symmetry, achiral) should rapidly interconvert to the very likely somewhat more stable twist conformation[1] **a** (D_2 symmetry) or its mirror image **c** (D_2 symmetry), respectively. In the present communication we describe a synthesis of this novel hydrocarbon **19**[2][3] *(Scheme 2)*.

Scheme 1



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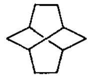
[1] An example where the twist conformation is actually preferred is the rigid compound twistane (**d**) [1].

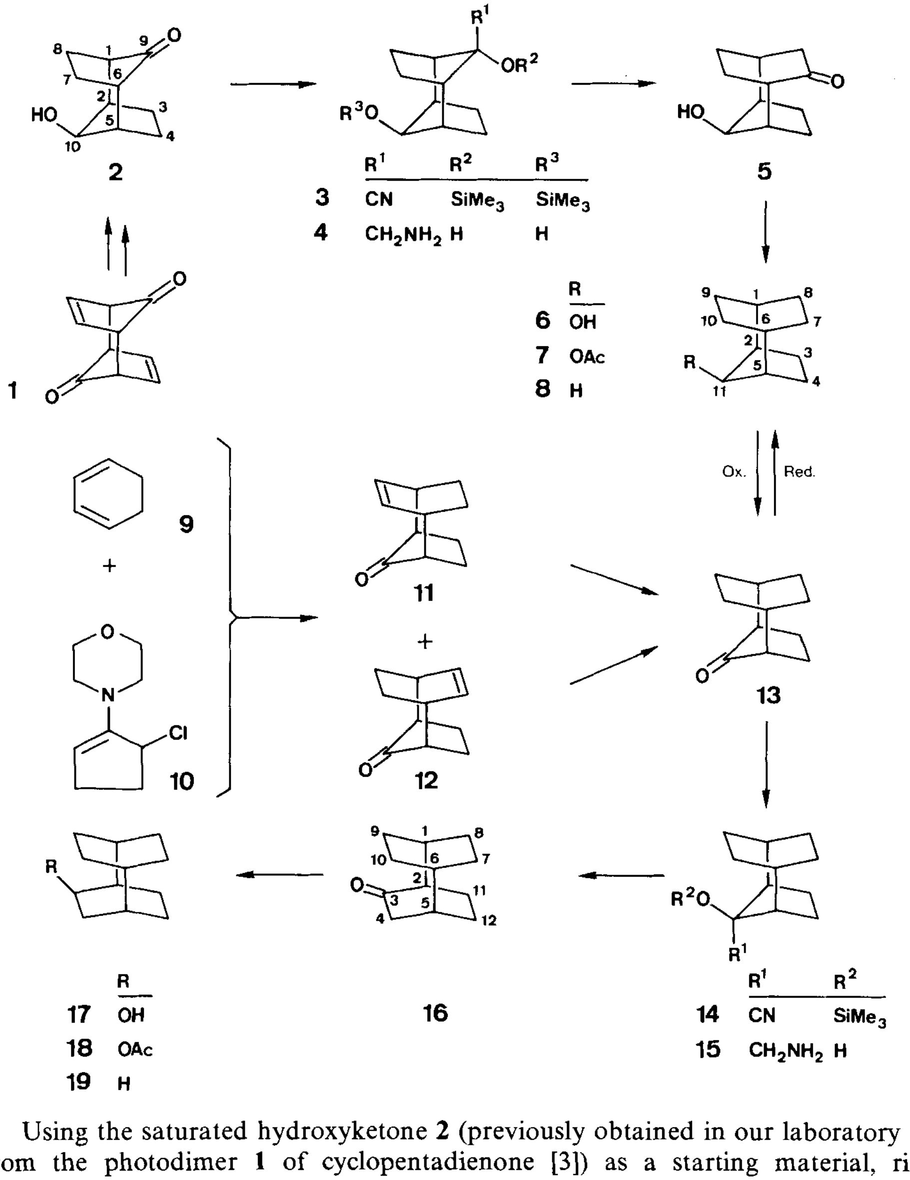


d

[2] These results were first presented by us at the meeting of the Swiss Chemical Society (Schweizerische Chemische Gesellschaft) on October 7, 1977, in Berne.

[3] To obtain conformational information, the equilibrium **a**$\rightleftarrows$**b**$\rightleftarrows$**c** (**19**) is under investigation. The results will be published in a forthcoming paper.

Scheme 2



Using the saturated hydroxyketone **2** (previously obtained in our laboratory [2] from the photodimer **1** of cyclopentadienone [3]) as a starting material, ring enlargements of the cyclopentanone rings each by one carbon atom were achieved applying twice the method of *Tiffeneau-Demjanov* [4]. Cyanosilylation [5] of **2** yielded the protected cyanohydrine **3**[4]) [IR. (CCl_4): 2228; ^{1}H-NMR.: 0.10 (*s*, *endo*-$(H_3C)_3$Si-O-C(9)); 0.26 (*s*, *endo*-$(H_3C)_3$Si-O-C(10)); 3.70 (*t*, $J_{2,exo\text{-}10}$ and $J_{5,exo\text{-}10}$ each = 3,

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[4]) **3** and all the compounds described hereafter have been characterized spectroscopically (IR.: $\tilde{\nu}_{max}$ in cm^{-1}; ^{1}H- and ^{13}C-NMR.: $CDCl_3$ as solvent, chemical shifts are reported in δ units relative to internal TMS, δ 0.00 ppm, coupling constants are given in Hz), all m.p. are uncorrected.

exo-H-C(10))]. Reduction with lithium aluminium hydride gave upon normal work-up directly the *β*-amino-alcohol **4**. Treatment of **4** · **HCl** with sodium nitrite in aqueous acetic acid afforded the ring enlarged hydroxyketone **5** [IR. ($CHCl_3$): 3612, 3450, 1706; ^{1}H-NMR.: 4.12 (*t*, $J_{2,exo\text{-}11}$ and $J_{5,exo\text{-}11}$ each=3.5, *exo*-H-C(11))]. Converting the hydroxyketone **5** to the alcohol **6** was best achieved (73.5% or 82% relative to converted starting material) by electrochemical reduction using a Pb-cathode in sulfuric acid/methanol. Oxidation of the alcohol **6** with chromic acid in acetone afforded the ketone **13**. The latter could also be synthesized by a different route: Cycloaddition of the allylic cation generated from 5-chloro-1-morpholinocyclopentene (**10**) to cyclohexa-1,3-diene (**9**)[5]) gave a separable mixture of *anti*- and *syn*-tricyclo[4.2.2.1^{2,5}]undec-7-en-11-one[6]) (**11**: m.p. 209-211° and **12**: m.p. 198-200°, respectively) in the ratio 93:7. Their structures were assigned especially by ^{1}H-NMR.-spectroscopy using $Eu(dpm)_3$ shift reagent. Catalytic hydrogenation of **11** as well as **12** yielded the saturated ketone **13**, which could be reduced with lithium aluminum hydride to the alcohol **6** *(vide supra)*. The hydrocarbon **8**, tricyclo[4.2.2.1^{2,5}]undecane, m.p. 210-214° [^{13}C-NMR.: 23.08, 27.03 and 27.38 (each 2*t*, C(3), C(4), C(7), C(8), C(9) and C(10)); 30.85 (2*d*, C(1) and C(6)); 35.21 (*t*, C(11)); 40.08 (2*d*, C(2) and C(5))] was obtained (24% or 91.5% relative to converted starting material) by photochemical reduction of the acetate **7** according to a procedure recently described by *Pète et al.* [7].

For the synthesis of the title compound **19** the second 5-membered ring had also to be enlarged by one carbon atom. By the same reaction sequence as described above (**2**→**3**→**4**→**5**) the ketone **13** was transformed *via* the cyanotrimethylsilyloxy compound **14** and the *β*-amino-alcohol **15** to the ring enlarged ketone **16** [IR. ($CHCl_3$): 1698]. $LiAlH_4$ reduction (→**17**), acetylation (→**18**) and subsequent photolysis yielded (53% or 65% relative to converted starting material) the novel hydrocarbon tricyclo[4.2.2.2^{2,5}]dodecane (**19**), m.p. 242-248° [^{13}C-NMR.: 24.33 (8*t*, C(3), C(4), C(7), C(8), C(9), C(10), C(11) and C(12)); 29.72 (4*d*, C(1), C(2), C(5) and C(6)).

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[5]) The reaction was carried out in analogy to the cycloaddition to cyclopentadiene as elaborated by *R. Schmid & H. Schmid* [6].

[6]) The *anti/syn*-nomenclature indicates the relative position of the carbonyl function and the double bond.