101. *Anti*- and *syn*-Tricyclo[4.2.1.$1^{2,5}$]decane[1])

Preliminary communication

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Summary

The two novel tricyclic $C_{10}H_{16}$ compounds *anti*- and *syn*-tricyclo[4.2.1.$1^{2,5}$]-decane (**16** and **17**, respectively) were synthesized starting either from the photodimer **2** (*anti*) or the two cycloaddition products **8** (*anti*) and **9** (*syn*).

In the present communication we describe syntheses of *anti*- and *syn*-tricyclo-[4.2.1.$1^{2,5}$]decane (**16** and **17**, respectively), two hitherto unknown members of the set of tricyclic $C_{10}H_{16}$ cage compounds, which have attracted the interest of several authors because of their structural relation to adamantane [1].

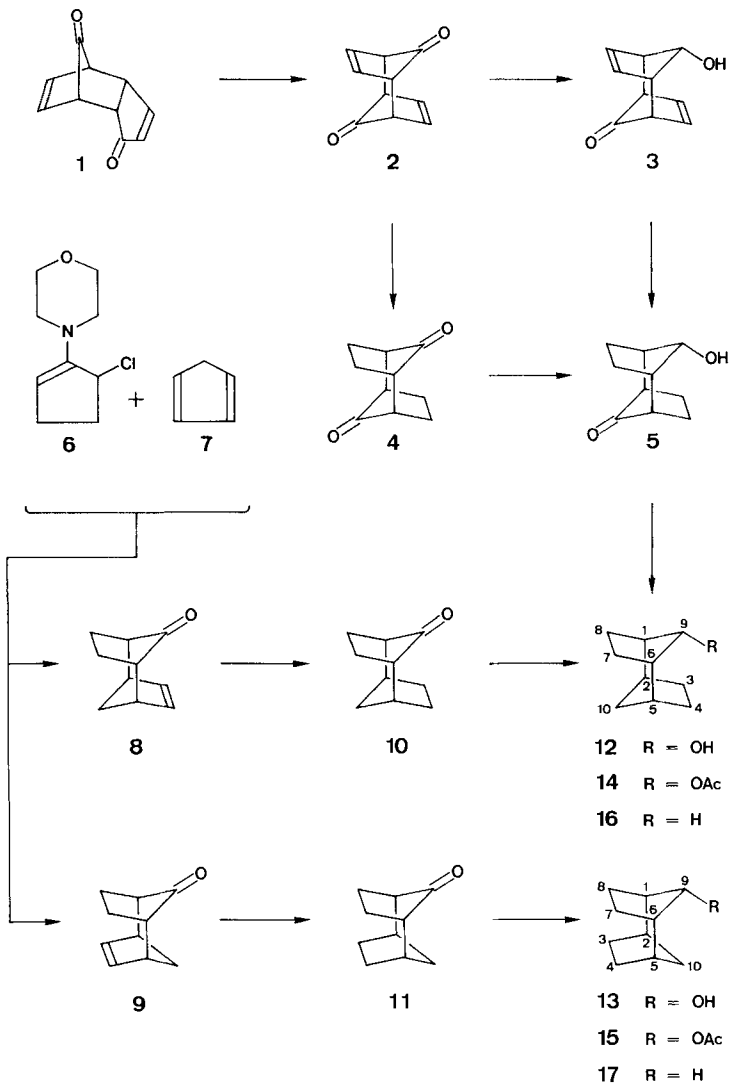
For the preparation of the *anti*-compound **16** as sole product, *anti*-tricyclo-[4.2.1.$1^{2,5}$]deca-3,7-dien-9,10-dione (**2**), obtained in our laboratory upon irradiation of the dimer **1** of cyclopentadienone [2], was chosen as suitable starting material. Reduction of **2** with sodium borohydride in a mixture of methanol and water at ambient temperature for one hour gave exclusively and in quantitative yield the unsaturated ketoalcohol **3**, which was hydrogenated in the presence of 5% Pd/C as catalyst to the saturated ketoalcohol **5**. The latter was also obtained almost quantitatively by first hydrogenating **2** to the known saturated diketone **4** [2] and subsequent sodium borohydride reduction if quenched after 10 minutes.

Converting **5** to the alcohol **12**, *i.e.* removal of the carbonyl oxygen, was best achieved (73.5% or 81% relative to converted starting material) by electrochemical reduction using a Pb-cathode in sulfuric acid/methanol. *Anti*-Tricyclo[4.2.1.$1^{2,5}$]-decane (**16**) was finally obtained (49.5% or 97% relative to converted starting material) by photochemical reduction of the corresponding acetate **14** according to a procedure recently described by *Pète et al.* [3].

Both the *anti*- and *syn*-compounds **16** and **17** can be prepared starting from 5-chloro-1-morpholinocyclopentene (**6**) and cyclopentadiene (**7**): cycloaddition of the allylic cation generated from the chlorinated enamine to the diene gives a separable mixture of *anti*- and *syn*-tricyclo[4.2.1.$1^{2,5}$]dec-3-en-9-one (**8** and **9**, respectively) in the ratio of 88:12 [4]; the *anti*-isomer **8** was transformed to the

[1]) The *anti*/*syn*-nomenclature indicates the relative position of the two methylene bridges.

Scheme



alcohol **12** (*vide supra*) by catalytic hydrogenation (→**10**) followed by lithium aluminum hydride reduction.

By the same reaction sequence the *syn*-isomer **9** yielded *via* the saturated ketone **11** the alcohol **13**. The hydrocarbon **17**, *syn*-tricyclo[4.2.1.$1^{2,5}$]decane, was obtained by acetylation and subsequent photochemical reduction of the acetate **15** (45% or 86% relative to converted starting material) in analogy to the above described transformation **12**→**14**→**16**.

Table. *Dates of* anti- *and* syn-*tricyclo*[4.2.1.$1^{2,5}$]*decane* (**16** *and* **17**).

		16	**17**
M.p.		142–145°	164–167°
^{13}C-NMR. (25 MHz, $CDCl_3$)	C(3),C(4),C(7),C(8)	29.27 (4*t*)	25.78 (4*t*)
	C(9),C(10)	33.59 (2*t*)	29.56 (2*t*)
	C(1),C(2),C(5),C(6)	39.59 (4*d*)	36.02 (4*d*)
^{1}H-NMR. (100 MHz, $CDCl_3$)	*exo*-H–C(9), *exo*-H–C(10)	0.90 (*m*, $w_{1/2}$ = 19, among others J_{gem} = 11)	0.45 (*m*, $w_{1/2}$ = 16, among others J_{gem} = 12)
	exo-H–C(3), *exo*-H–C(4), *exo*-H–C(7), *exo*-H–C(8)	1.1–1.8 (*m*)	0.7–1.4 (*m*)
	endo-H–C(3), *endo*-H–C(4), *endo*-H–C(7), *endo*-H–C(8)		1.3–2.0 (*m*)
	endo-H–C(9), *endo*-H–C(10)	1.8–2.1 (*m*)	
	H–C(1), H–C(2), H–C(5), H–C(6)		2.0–2.5 (*m*)

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