Synthesis of Ufolene

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An eight-step synthesis of the tricyclic hydrocarbon ufolene (15) is described. The configuration of ufolene and two intermediates is secured by X-ray analysis.

Synthese von Ufolen

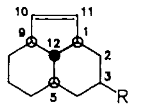
Eine Achtstufen-Synthese des tricyclischen Kohlenwasserstoffes Ufolen (15) wird beschrieben. Die Konfiguration von Ufolen und zweier Zwischenprodukte wird durch Röntgenstrukturanalyse gesichert.

In connection with our investigations on the regioselectivity of free-radical additions to alkenes[3a)] we were interested in the synthesis of (1α,5α,9α,12β)-tricyclo[7.2.1.0^{5,12}]-dodec-10-enes **1** with different equatorial substituents in position 3. Models of **1** with R = H resemble with some imagination interstellar crafts; therefore, we propose the trival name ufolene for the parent hydrocarbon (1α,5α,9α,12β)-tricyclo[7.2.1.0^{5,12}]dodec-10-ene (**15**). The saturated hydrocarbon should have consequently the name ufolane[3b)]. To our knowledge ufolene has not been described previously. Our initial efforts were therefore directed to the synthesis of the unsubstituted ufolene itself.

Reduction of Acenaphthene Derivatives

At first sight, a convenient method for the synthesis of ufolene should consist in the hydrogenation of easily accessible 1-substituted or 1,2-disubstituted acenaphthenes and subsequent formation of the double bond by elimination reactions. But on catalytic hydrogenation of 1-aminoacenaphthene (**2a**) only partial hydrogenation of the rings took place and the functional group was split off, 2a,3,4,5-tetrahydroacenaphthene (**3**, 79%) being formed. With rhodium as a catalyst, benzylalcohols can be hydrogenated to cyclohexylcarbinols[4a)], but in the case of 1-hydroxy-acenaphthene (**2b**) no hydrogenation could be effected with this catalyst.

Better results were obtained with platinum as catalyst in the case of 1,2-dihydroxyacenaphthene (**4**). A *cis/trans* mixture of **4** yielded on hydrogenation at atmospheric pressure (8 h) 2a,3,4,5-tetrahydro-1,2-dihydroxy-acenaphthene (**5**). Prolonged hydrogenation (68 h) led to a mixture of four stereoisomers of **6** [**6a–d**, 85%, R_f = 0.35, 0.30, 0.24, and 0.10, respectively, dichloromethane/acetone (4:1)]. They could be separated by medium-pressure chromatography. Their constitution follows from the mass, ^{13}C-NMR, and ^{1}H-NMR spectra and the elemental analyses. The main product **6d** could be isolatd by fractional crystallisation from methanol in 17% yield. In **6d** the hydroxy groups possess *trans* configuration and in **6a–c** *cis* configuration. This could be shown by hydrogenation of pure stereoisomers of **4**, which were obtained by reduction of acenaphthenequinone with lithium tetrahydridoaluminate (→*cis*-**4**) and sodium tetrahydridoborate (→*trans*-**4**), respectively. But with respect to the desired carbon skeleton, **6d** has the wrong stereochemistry. As the X-ray analysis shows (Fig. 1), the two six-membered rings are *cis*-connected. Therefore, a total synthesis of **15** was planned.



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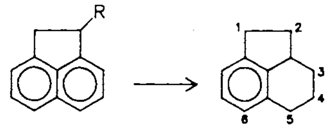
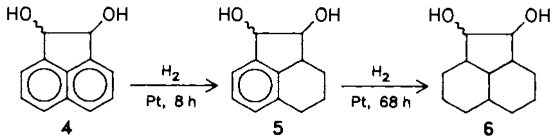


2a: R = NH$_2$
b: R = OH

3



4 5 6

Total Synthesis

The synthesis of **15** should be possible starting with the tetralindicarboxylic acid **7**, stereochemically appropriate reduction of the aromatic ring, and consecutive formation of the five-membered ring by acyloin condensation in the sterically favourable *cis* arrangement. As shown in the Scheme, the acyloin condensation and the following reduction took a surprising course, but in the last reduction step the correct stereochemistry was obtained.

Birch reduction (sodium/liquid ammonia) of the tetralindicarboxylic acid **7** yielded the hexahydronaphthalenedicarboxylic acid **8** in low yield only. Better results (74%) were obtained with lithium in liquid ammonia. Acyloin condensation of the ester **10**, which was obtained by catalytic hy-

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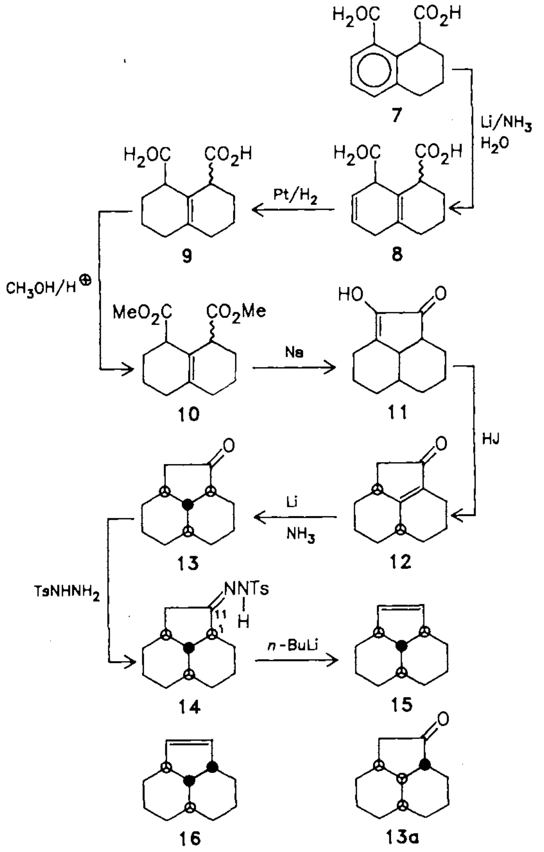
drogenation of **8** and esterification, as well as *trans* reduction of the 9,10-double bond should be possible with sodium. But treatment of **10** with sodium in liquid ammonia with ether as cosolvent did not yield the expected acyloin but **11**. Usually an α-diketone is presumed as intermediate for the acyloin condensation. But the 5-membered cyclic α-diketone formed from **10** should show a very unfavorable dipole interaction between the two carbonyl groups. Therefore – as with 1,2-cyclopentandione[4b)] – only the enol form **11** may exist, which seems to be resistant against further reduction under the reaction conditions.

Scheme 2



Catalytic hydrogenation of **11** gave a compound identical with **6b**, in which the five-membered ring is *trans*-anellated. This can be concluded from the ^{13}C-NMR spectrum: As already mentioned, the hydroxy groups of **6b** have cis configuration. All *cis*-dihydroxy isomers of **6** with the desired *cis* anellation of the five-membered ring possess a plane of symmetry and should show only 7 ^{13}C-NMR signals, whereas those isomers with a *trans* anellation of the five-membered ring lack any element of symmetry, and should show 12 ^{13}C-NMR signals, which is the case for **6b**.

Reduction of **11** with hydroiodic acid formed **12**; its constitution as (5α,9α)-tricyclo[7.2.1.0^{5,12}]dodec-1(12)-en-11-one follows from the X-ray analysis of the tosylhydrazone (Fig. 2). The formation of the α,β-unsaturated ketone **12** including the migration of the double bond is paralleled by the course of the hydrogen iodide reduction of 3,5,5-trimethyl-1,2-cyclohexandione (or its enol form, respectively) described by Reusch et al[4c)]. A reaction mechanism is proposed by these authors.

For the conversion of **12** to **13**, *trans* addition of hydrogen to the double bond is needed. Lithium in liquid ammonia has been used for stereoselective *trans* reductions of α,β-unsaturated ketones[5)]. The formation of **13** instead of **13a** could be expected, because attack by the hydrogen donor at C-12 in the intermediate radical antion[6)] the β side should be sterically less hindered.

Reduction of **12** gave **13** as well as the corresponding alcohol, which was converted to **13** with PCC in 82% yield. Ketone **13** has the desired configuration. This was proven by X-ray analysis of the tosylhydrazone **14** (Fig. 3).

The conversion of **14** to **15** should be possible by a Shapiro reaction, which gives the less substituted alkene with two equivalents of alkyllithium compounds[7)]. The mechanism of the Shapiro reaction involves the formation of carbanions in α-position to the C–N double bond. Therefore, an epimerisation at C1 and the formation of **16** with a *trans*-anellated five-membered ring could not be excluded. The Shapiro reaction with **14** yielded an alkene (45%), which, judging from the analytical and spectral data, possesses the right constitution, and which showed only 7 ^{13}C-NMR signals. This excluded a structure with a *trans*-anellated five-membered ring as in **16** and also an isomer with a double bond between C1 and C11. Thus, the synthesis of ufolene (**15**) starting from **7** has been effected in an overall yield of about 10%.

X-Ray Analyses*)

Crystals of **6d** obtained by recrystallisation from dichloromethane are monoclinic, space group $C2/c$. The unit cell, which has the parameters $a = 2856.9(4)$, $b = 770.1(1)$, $c = 998.8(1)$ pm, and $\beta = 100.6(2)°$, contains 8 molecules yielding a calculated density of 1.207 g/cm^3. The data were collected at 293 K on a Syntex $P2_1$ diffractometer using Cu-K_α radiation ($\lambda = 154.178$ pm) with graphite monochromator in the Θ-2Θ mode in the range of $3° \leq 2\Theta \leq 135°$ at a scan speed between 2.93 and 29.30°/min depending on the intensity of the reflection.

The data were corrected for Lorentz and polarisation but not for absorption effects. The structure was solved by direct methods and difference Fourier syntheses. The positional parameters of the hydrogen atoms were refined together with isotropic temperature factors. The refinement using 1755 out of 1861 measured independent reflections [$I \geq 2.5\sigma(I)$] converged at $R = 0.042$. A final difference map displayed no electron density higher than $0.24 \cdot 10^6$ e/pm^3.

The two six-membered rings of **6d** show different conformations (Fig. 1). While ring I (C1–C5, C12) is in a flattened chair conformation, the *cis*-configurated ring II (C8–C12)

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*) Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53127, the names of the authors, and the journal citation.

has a twist form. The three rings are all *cis*-configurated at the bridgehead atoms.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters [Å^2], bond lengths [pm] and bond angles [°] of **6d** (for numbering of the atoms see Fig. 1)

	X/A	Y/B	Z/C	UEQ
C(1)	0.0686(1)	0.3528(2)	0.5476(2)	0.049(0)
C(2)	0.0714(1)	0.5037(2)	0.4498(2)	0.055(1)
C(3)	0.1056(1)	0.6437(2)	0.5142(2)	0.060(1)
C(4)	0.1555(1)	0.5707(2)	0.5574(2)	0.050(0)
C(5)	0.1567(1)	0.4234(2)	0.6598(1)	0.040(0)
C(6)	0.2021(0)	0.3130(2)	0.6754(1)	0.041(0)
C(7)	0.1924(0)	0.1923(2)	0.5526(1)	0.037(0)
C(8)	0.1396(0)	0.1457(2)	0.5377(1)	0.038(0)
C(9)	0.1151(1)	0.1290(2)	0.3888(1)	0.045(0)
C(10)	0.0610(1)	0.1096(2)	0.3704(2)	0.058(1)
C(11)	0.0395(1)	0.1987(3)	0.4822(2)	0.062(1)
C(12)	0.1177(0)	0.2853(2)	0.6186(1)	0.039(0)
O(1)	0.2449(0)	0.4073(2)	0.6760(1)	0.056(0)
O(2)	0.2230(0)	0.0445(1)	0.5679(1)	0.050(0)

C(2)-C(1)	153.0(2)	C(11)-C(1)	152.6(2)
C(12)-C(1)	154.0(2)	C(3)-C(2)	151.5(2)
C(4)-C(3)	152.0(2)	C(5)-C(4)	152.4(2)
C(6)-C(5)	153.3(2)	C(12)-C(5)	154.1(2)
C(7)-C(6)	152.3(2)	O(1)-C(6)	142.1(2)
C(8)-C(7)	153.2(2)	O(2)-C(7)	142.7(2)
C(9)-C(8)	152.7(2)	C(12)-C(8)	155.1(2)
C(10)-C(9)	153.0(2)	C(11)-C(10)	153.2(3)
C(11)-C(1)-C(2)	114.0(1)	C(12)-C(1)-C(2)	113.6(1)
C(12)-C(1)-C(11)	108.3(1)	C(3)-C(2)-C(1)	112.0(1)
C(4)-C(3)-C(2)	110.7(1)	C(5)-C(4)-C(3)	111.8(1)
C(6)-C(5)-C(4)	113.4(1)	C(12)-C(5)-C(4)	114.1(1)
C(12)-C(5)-C(6)	101.6(1)	C(7)-C(6)-C(5)	103.4(1)
O(1)-C(6)-C(5)	115.3(1)	O(1)-C(6)-C(7)	110.1(1)
C(8)-C(7)-C(6)	104.7(1)	O(2)-C(7)-C(6)	112.6(1)
O(2)-C(7)-C(8)	113.1(1)	C(9)-C(8)-C(7)	112.3(1)
C(12)-C(8)-C(7)	105.5(1)	C(12)-C(8)-C(9)	114.0(1)
C(10)-C(9)-C(8)	113.4(1)	C(11)-C(10)-C(9)	113.6(1)
C(10)-C(11)-C(1)	113.5(1)	C(5)-C(12)-C(1)	116.3(1)
C(8)-C(12)-C(1)	114.6(1)	C(8)-C(12)-C(5)	106.2(1)

In the crystal the molecules form chains connected by hydrogen bonds: O1 – H1 ··· O2, O1 – H1 84(2), O1 – O2 276.3, O2 – H1 192 pm; O2 – H2 ··· O1, O2 – H2 91(2), O1 – O2 278.2, O1 – H2 190 pm.

The bonding parameters are all very close to literature values (C – C 152 – 155 pm, C – O 142 – 143 pm, C – H 97 – 103 pm).

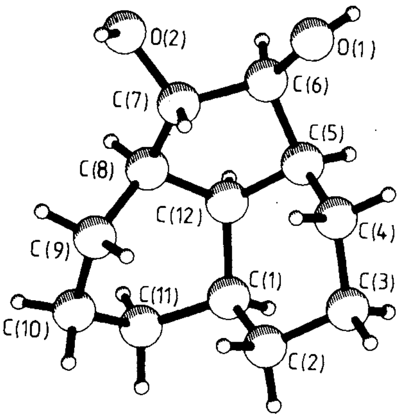

Figure 1. Structure of (1α,5α,9α,10α,11β,12α)-10,11-dihydroxytricyclo[7.2.1.0^{5,12}]dodecane (**6d**) from X-ray analysis

Crystals of the tosylhydrazone of **12** obtained by recrystallisation from methanol are monoclinic, space group $P2_1/c$. The unit cell, which has the parameters a = 2293.3(4), b = 1598.8(4), c = 999.6(3) pm, and β = 91.31(4)°, contains 8 molecules yielding a calculated density of 1.249 g/cm^3. Data collection and structure solution were performed as described for **6d**; hydrogen atom positions were calculated and refined isotropically together with their directly bonded atoms. The refinement using 3377 out of 4895 measured independent reflections $[F \geq 4.0\sigma(F)]$ converged at R = 0.079. A final difference map displayed no electron density higher than $0.36 \cdot 10^6$ e/pm^3.

In the analyses of **6d** and of the tosylhydrazone of **12** the program SHELX-76[8] and own programs were used. Complex atom-scattering factors[9a] were employed.

The tosylhydrazone of **12** crystallises with two molecules in the asymmetric unit. The two crystallographically independent molecules show only small differences in their geometry.

As expected, the double bonds C2 – C12 and C1 – N2 cause a significant flattening of the five-membered ring compared with compound **6d**. Whereas the largest deviations from the best plane of the five-membered ring in **6d** are near 27 pm, they are only 8 pm in the tosylhydrazone of **12**. The six-membered ring II (C6 – C10, C12) has a chair conformation, which is only slightly distorted due to the sp^2-hybridisation of C12, whereas ring I (C2 – C6, C12) deviates only at C4 and C5 from the planarity, which is caused by the double bond C2 – C12. The bond distances of the double bonds are 132 pm (C2 – C12) and 128 pm (C1 – N2), respectively. The nitrogen atom N1 is flattened with respect to the tetrahedral geometry but is still nonplanar (sum of angles, mean of the two crystallographically independent molecules: 349°). The bond distances between the two nitrogen atoms (142 pm) like the other bonding parameters are in their usual range.

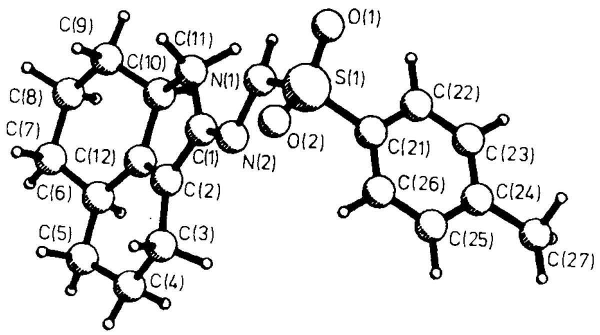

Figure 2. Structure of the tosylhydrazone of **12** from X-ray analysis

The tosylhydrazone **14** crystallises from methanol in the orthorhombic space group *Pbca* with a = 1003.3(6), b = 1588.8(3), c = 2336.5(8) pm, $V = 3724.50 \cdot 10^6$ pm^3, Z = 8, d_{cal} = 0.94 g/cm^3, μ = 1.38 cm^{-1}. The intensities of 2516 unique reflections in the range of $3° \leq 2\Theta \leq 45°$ were measured on a Siemens AED 2 diffractometer (Mo-K_α radiation, graphit monochromator). Of these reflexions 680 with $I \leq 2\sigma(I)$ were classified unobserved. The structure was solved by direct methods using SHELX 76. Full-matrix least-squares refinement with anisotropic temperature factors for all nonhydrogen atoms leads to a final R value of 0.070 (R_w = 0.061). Most of the hydrogen atoms were fixed at there carbon atoms and refined together with them as

Table 2. Atomic coordinates and equivalent isotropic thermal parameters [Å^2], bond lengths [pm] and bond angles [°] of the tosyl hydrazone of **12** (for numbering of the atoms see Fig. 2)

	X/A	Y/B	Z/C	UEQ
S(1)	0.0697(1)	0.2319(1)	0.7344(2)	0.065(1)
O(1)	0.0415(2)	0.3099(3)	0.7505(5)	0.086(2)
O(2)	0.0872(2)	0.2051(3)	0.6048(4)	0.081(2)
N(1)	0.1285(2)	0.2401(3)	0.8319(5)	0.062(2)
N(2)	0.1650(2)	0.1678(3)	0.8345(5)	0.058(2)
C(1)	0.2069(2)	0.1744(4)	0.9198(6)	0.058(2)
C(2)	0.2512(2)	0.1102(4)	0.9371(6)	0.062(2)
C(12)	0.2883(3)	0.1312(5)	1.0328(7)	0.085(3)
C(10)	0.2700(3)	0.2102(5)	1.1080(8)	0.070(3)
C(11)	0.2213(3)	0.2450(4)	1.0151(6)	0.072(2)
C(3)	0.2560(3)	0.0305(4)	0.8613(7)	0.075(3)
C(4)	0.3019(4)	-0.0257(5)	0.9203(10)	0.142(5)
C(5)	0.3526(3)	0.0142(5)	0.9811(9)	0.104(4)
C(6)	0.3414(3)	0.0848(5)	1.0754(9)	0.106(4)
C(9)	0.3199(3)	0.2634(5)	1.1373(9)	0.101(3)
C(8)	0.3718(3)	0.2164(5)	1.1986(7)	0.088(3)
C(7)	0.3872(3)	0.1411(5)	1.1136(10)	0.120(4)
C(21)	0.0233(2)	0.1547(4)	0.7952(5)	0.055(2)
C(22)	-0.0083(3)	0.1719(4)	0.9100(6)	0.072(3)
C(23)	-0.0466(3)	0.1124(5)	0.9547(6)	0.073(3)
C(24)	-0.0559(3)	0.0380(4)	0.8871(6)	0.066(2)
C(25)	-0.0234(3)	0.0210(5)	0.7763(6)	0.073(3)
C(26)	0.0154(3)	0.0805(4)	0.7304(6)	0.066(2)
C(27)	-0.0993(3)	-0.0244(5)	0.9394(7)	0.094(3)
C(10)"	-0.2877(0)	-0.2287(0)	-0.0200(0)	0.055(14)
S(1)'	0.5682(1)	0.2258(1)	0.1478(1)	0.061(1)
O(1)'	0.5871(2)	0.2226(3)	0.2844(4)	0.073(2)
O(2)'	0.5392(2)	0.1546(3)	0.0887(4)	0.076(2)
N(1)'	0.6262(2)	0.2378(3)	0.0578(6)	0.061(2)
N(2)'	0.6611(2)	0.3079(3)	0.0945(4)	0.059(2)
C(1)'	0.7064(2)	0.3172(4)	0.0228(6)	0.059(2)
C(2)'	0.7465(2)	0.3841(4)	0.0452(6)	0.065(2)
C(12)'	0.7874(3)	0.3815(5)	-0.0458(8)	0.089(3)
C(10)'	0.7766(3)	0.3136(5)	0.1531(8)	0.075(4)
C(11)'	0.7257(3)	0.2637(5)	-0.0932(6)	0.078(3)
C(9)'	0.8311(3)	0.2663(6)	-0.1783(8)	0.115(4)
C(8)'	0.8816(3)	0.3233(6)	-0.2042(9)	0.127(5)
C(7)'	0.8909(3)	0.3846(7)	-0.0868(13)	0.149(6)
C(6)'	0.8397(3)	0.4375(6)	-0.0504(10)	0.119(4)
C(5)'	0.8426(4)	0.4919(6)	0.0701(11)	0.129(5)
C(4)'	0.7876(5)	0.5170(6)	0.1200(11)	0.143(5)
C(3)'	0.7448(3)	0.4494(4)	0.1488(7)	0.089(3)
C(21)'	0.5225(2)	0.3132(4)	0.1300(5)	0.055(2)
C(22)'	0.4880(2)	0.3203(4)	0.0127(6)	0.062(2)
C(23)'	0.4506(3)	0.3869(4)	0.0006(6)	0.068(2)
C(24)'	0.4466(3)	0.4474(4)	0.1003(7)	0.073(3)
C(25)'	0.4813(3)	0.4390(4)	0.2136(6)	0.075(3)
C(26)'	0.5202(3)	0.3725(4)	0.2298(6)	0.068(2)
C(27)'	0.4039(3)	0.5194(4)	0.0865(8)	0.092(3)
C(10)'	-0.7902(0)	-0.2853(0)	0.0672(0)	0.109(22)

C(2)-C(1)	145.2(8)	C(11)-C(1)	150.9(9)
C(12)-C(2)	130.9(9)	C(3)-C(2)	148.8(9)
C(10-C(12)	153.3(11)	C(6)-C(12)	148.0(10)
C(11)-C(10)	153.9(9)	C(9)-C(10)	144.9(10)
C(4)-C(3)	149.5(11)	C(5)-C(4)	144.7(12)
C(6)-C(5)	149.6(12)	C(7)-C(6)	142.8(11)
C(8)-C(9)	152.5(10)	C(7)-C(8)	152.2(12)
C(2)'-C(1)'	142.4(8)	C(11)'-C(1)'	151.5(9)
C(12)'-C(2)'	132.2(9)	C(3)'-C(2)'	147.3(9)
C(10)'-C(12)'	154.3(11)	C(6)'-C(12)'	149.8(11)
C(11)'-C(10)'	154.5(10)	C(9)'-C(10)'	148.6(11)
C(8)'-C(9)'	150.1(12)	C(7)'-C(8)'	154.0(15)
C(6)'-C(7)'	149.9(13)	C(5)'-C(6)'	148.6(15)
C(4)'-C(5)'	142.4(14)	C(3)'-C(4)'	149.3(12)
C(11)-C(1)-C(2)	108.1(5)	C(12)-C(2)-C(1)	110.3(6)
C(3)-C(2)-C(1)	127.2(5)	C(3)-C(2)-C(12)	122.6(6)
C(10)-C(12)-C(2)	112.9(6)	C(6)-C(12)C-(2)	126.7(7)
C(6)-C(12)-C(10)	120.3(6)	C(11)-C(10)-C(12)	101.8(6)
C(9)-C(10)-C(12)	111.1(6)	C(9)-C(10)-C(11)	117.9(6)
C(10)-C(11)-C(1)	104.8(5)	C(4)-C(3)-C(2)	111.9(6)
C(5)-C(4)-C(3)	116.9(7)	C(6)-C(5)-C(4)	116.7(7)
C(5)-C(6)-C(12)	110.4(7)	C(7)-C(6)-C(12)	110.7(7)
C(7)-C(6)-C(5)	120.4(7)	C(8)-C(9)-C(10)	113.5(7)
C(7)-C(8)-C(9)	110.6(6)	C(8)-C(7)-C(6)	118.0(6)
C(11)'-C(1)'-C(2)'	110.2(5)	C(12)'-C(2)'-C(1)	109.6(6)
C(3)'-C(2)'-C(1)'	128.0(5)	C(3)'-C(2)'-C(12)'	122.4(6)
C(10)'-C(12)'-C(2)'	113.2(6)	C(6)'-C(12)'-C(2)'	125.8(7)
C(6)'-C(12)'-C(10)'	121.0(7)	C(11)'-C(10)'-C(12)'	101.9(6)
C(9)'-C(10)'-C(12)'	110.7(6)	C(9)'-C(10)'-C(11)'	116.6(7)
C(10)'-C(11)'-C(1)'	103.9(6)	C(8)'-C(9)'-C(10)'	112.1(8)
C(7)'-C(8)'-C(9)'	110.5(7)	C(6)'-C(7)'-C(8)'	116.6(8)
C(7)'-C(6)'-C(12)'	107.6(8)	C(5)'-C(6)'-C(12)'	110.2(7)
C(5)'-C(6)'-C(7)'	120.4(8)	C(4)'-C(5)'-C(6)'	115.2(8)
C(3)'-C(4)'-C(5)'	117.1(8)	C(4)'-C(3)'-C(2)	110.5(7)

rigid groups. The ratio no. of parameters/no. of *F* values was 1/7.5.

As expected, the saturated ring system of **14** shows no distortion; the two *trans*-anellated six-membered rings possess the chair conformation and the *cis* anellated five-membered ring the envelope form.

Table 3. Atomic coordinates and equivalent isotropic thermal parameters [Å^2], bond lengths [pm] and bond angles [°] of **14** (for numbering of the atom see Fig. 3)

Atom	x	y	z	B
S	0.2599(1)	0.24019(8)	0.08426(5)	4.48(6)
O(1)	0.2778(4)	0.3223(2)	0.0614(1)	6.3(2)
O(2)	0.1308(3)	0.2124(2)	0.1027(1)	6.0(2)
N(1)	0.3577(4)	0.2391(3)	0.1406(2)	4.2(2)
N(2)	0.3622(4)	0.1618(2)	0.1700(2)	4.3(2)
C(1)	0.3166(4)	0.1669(3)	0.0340(2)	3.64(9)
C(2)	0.2440(6)	0.0962(3)	0.0281(2)	4.8(1)
C(3)	0.2886(5)	0.0409(3)	-0.0205(2)	5.2(1)
C(4)	0.4039(5)	0.0567(3)	-0.0502(2)	4.5(1)
C(5)	0.4766(5)	0.1259(3)	-0.0365(2)	4.9(1)
C(6)	0.4338(5)	0.1831(3)	0.0050(2)	4.7(1)
C(7)	0.4510(6)	-0.0017(3)	-0.0977(2)	6.6(3)
C(8)	0.4448(5)	0.1623(3)	0.2121(2)	4.2(2)
C(9)	0.5309(5)	0.2351(3)	0.2340(2)	5.2(3)
C(10)	0.4663(6)	0.0879(3)	0.2497(2)	5.9(3)
C(11)	0.5159(5)	0.1251(3)	0.3023(2)	4.4(3)
C(12)	0.3638(6)	0.0208(3)	0.2584(3)	6.1(3)
C(13)	0.6434(6)	0.2492(4)	0.3346(2)	6.5(3)
C(14)	0.6054(6)	0.1974(4)	0.2847(2)	5.9(3)
C(15)	0.5618(6)	0.0698(4)	0.3500(2)	6.0(3)
C(16)	0.4581(8)	0.0027(4)	0.3599(3)	8.2(4)
C(17)	0.6059(7)	0.1225(5)	0.3995(2)	8.2(4)
C(18)	0.6956(7)	0.1959(5)	0.3828(3)	7.3(4)
C(19)	0.4055(7)	-0.0387(3)	0.3070(3)	7.6(4)

C(9)-C(8)	153.2 (0.7)	C(10)-C(8)	149.0 (0.7)
C(14)-C(9)	152.3 (0.8)	C(11)-C(10)	145.2 (0.7)
C(12)-C(10)	149.5 (0.8)	C(14)-C(11)	151.4 (0.8)
C(15)-C(11)	149.1 (0.7)	C(19)-C(12)	153.5 (0.9)
C(14)-C(13)	147.7 (0.8)	C(18)-C(13)	150.3 (0.9)
C(16)-C(15)	150.7 (0.9)	C(17)-C(15)	149.5 (0.9)
C(19)-C(16)	149.7 (1.0)	C(18)-C(17)	152.4 (1.0)
C(9)-C(8)-N(2)	128.7 (0.5)	C(10)-C(8)-N(2)	122.6 (0.5)
C(10)-C(8)-C(9)	108.7 (0.5)	C(14)-C(9)-C(8)	103.9 (0.4)
C(11)-C(10)-C(8)	103.0 (0.5)	C(12)-C(10)-C(8)	123.1 (0.5)
C(12)-C(10)-C(11)	114.3 (0.6)	C(14)-C(11)-C(10)	106.4 (0.5)
C(15)-C(11)-C(10)	119.8 (0.5)	C(15)-C(11)-C(14)	117.8 (0.5)
C(19)-C(12)-C(10)	110.6 (0.5)	C(18)-C(13)-C(14)	111.6 (0.6)
C(11)-C(14)-C(9)	102.6 (0.4)	C(13)-C(14)-C(9)	121.4 (0.6)
C(13)-C(14)-C(11)	111.2 (0.5)	C(16)-C(15)-C(11)	108.6 (0.5)
C(17)-C(15)-C(11)	109.8 (0.5)	C(17)-C(15)-C(16)	118.7 (0.6)
C(19)-C(16)-C(15)	115.3 (0.6)	C(18)-C(17)-C(15)	113.9 (0.6)
C(17)-C(18)-C(13)	114.6 (0.6)	C(16)-C(19)-C(12)	115.9 (0.5)

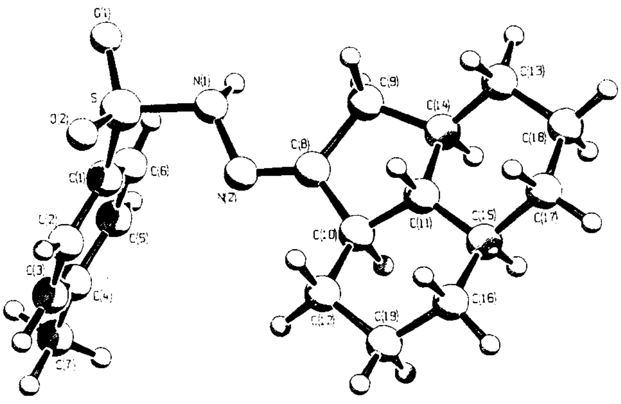

Figure 3. Structure of the tosylhydrazone **14** from X-ray analysis (SCHAKAL[9b])

Acknowledgement is made to the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft* for support of this work.

Experimental

Thin layer chromatography: SIL G/UV 254 sheets, Macherey-Nagel, dichloromethane/acetone (4:1).

Hydrogenation of 1-Aminoacenaphthene (**2a**): A mixture of 20.0 g (118 mmol) of **2a** and 1.6 g of Raney nickel was shaken for 2 h at

180°C under hydrogen (200 bar) until the uptake of hydrogen stopped. Distillation of the filtrate yielded 14.8 g (79%) 2a,3,4,5-tetrahydroacenaphthene, b.p. 129°C/26 mbar (ref.[10] 258°C/958 mbar). – MS (70 eV): m/z (%) = 158 (63) [M^+], 130 (100) [$M^+ - C_2H_4$].

trans-1,2-Dihydroxyacenaphthene (*trans*-**4**): A suspension of 25.0 g (137 mmol) of acenaphthenequinone in 700 ml of tetrahydrofuran was added dropwise within 5 h to a stirred solution of 11.0 g (291 mmol) of sodium tetrahydroborate in 250 ml of tetrahydrofuran (not dried). After stirring for 12 h, the mixture was acidified with dilute sulfuric acid and extracted with ether. The evaporation residue of the washed and dried ether phase yielded after recrystallisation from dichloromethane 18.05 g (71%) of *trans*-**4**, m.p. 149°C (uncorr.) (ref.[11] 160–163°C), TLC: R_f = 0.17. – ^{1}H NMR ([D$_6$]dimethyl sulfoxide): δ = 5.19 (s, 1H, OH), 5.83 [s, 1H, C*H*(OH)], 7.45 (d, J = 6 Hz, 1H, 3,8-H), 7.58 (dd, J = 6 and 9 Hz, 1H, 4,7-H), 7.77 (d, J = 9 Hz, 1H, 5,6-H). – MS (70 eV): m/z (%) = 186 (79) [M^+], 168 (95) [$M^+ - H_2O$), 140 (100).

2a,3,4,5-Tetrahydro-1,2-dihydroxyacenaphthene (**5**): 3.0 g (16.1 mmol) of a *cis*/*trans* mixture of **4**[12] in 200 ml of acetic acid was shaken for 8 h at room temp. with 50 mg of platinum dioxide under hydrogen (3 bar). Evaporation of the filtrate yielded after recrystallisation from dichloromethane 2.73 g (91%) of **5**, m.p. 207°C. – ^{1}H NMR ([D$_6$]dimethyl sulfoxide): δ = 0.93–2.83 (m, 4H, 2a,3,4,5-H), 3.57 (dd, J = 8 Hz, 1H, 2-H), 4.79 (d, J = 7.5 Hz, 1H, 1-H), 6.77–7.14 (m, 3H, 6,7,8-H). – MS (70 eV): m/z (%) = 190 (53) [M^+], 172 (81) [$M^+ - H_2O$], 144 (100) [$M^+ - H_2O - CO$).

$C_{12}H_{14}O_2$ (190.2) Calcd. C 75.76 H 7.42
Found C 75.41 H 7.44

10,11-Dihydroxytricyclo[7.2.1.0^{5,12}]dodecanes (**6a–d**): 6.55 g (35.2 mmol) of a *cis*/*trans* mixture of **4**[12] in 250 ml of acetic acid was shaken for 68 h at room temp. with 200 mg of patinum dioxide under hydrogen (3 bar). The evaporation residue of the filtrate yielded after recrystallisation from dichloromethane 5.86 g (85%) of **6** as a mixture of four stereoisomers **6a–d** (TLC: R_f = 0.35, 0.30, 0.24, and 0.10), which could be separated by medium-pressure chromatography using LiChroprep Si 60, 25–40 µm (Merck) with dichloromethane/acetone (4:1). **6d** could also be obtained (17%) by repeated recrystallisation from methanol of the crude mixture of stereoisomers obtained by hydrogenation of **4**. – ^{1}H NMR ([D$_6$]dimethyl sulfoxide, D_2O added): **6a**: δ = 1.18–1.93 (m), 3.35 (s), 3.83 (s), 4.14 (m). **6b**: δ = 0.89 (m), 1.07–1.99 (m), 3.34 (t, J = 7.5 Hz), 3.44 (s), 3.89 (t, J = 7.5 Hz). **6c**: δ = 1.03–1.82 (m), 2.31 (dd, J = 7.5 Hz), 3.59 (m), 4.30 (m). **6d**: δ = 0.81 (m), 0.99–1.73 (m), 1.83 (m), 2.11 (m), 3.47 (m), 3.70 (t, J = 7.5 Hz), 4.60 (dd, J = 7.5 Hz). – ^{13}C NMR ([D$_6$]dimethyl sulfoxide): **6a**: δ = 20.64, 21.27, 27.73, 30.72, 36.27, 40.32, 73.73. **6b**: δ = 21.26, 21.76, 25.07, 25.20, 29.93, 30.86, 33.24, 39.80, 41.11, 41.39, 69.75, 74.61. **6c**: δ = 19.85, 25.48, 27.73, 30.50, 35.77, 43.14, 77.22. **6d**: δ = 17.40, 23.53, 23.82, 25.09, 25.34, 29.76, 30.72, 34.71, 40.82, 41.64, 78.99, 82.68. – MS (70 eV): **6a**: m/z (%) = 196 (60), [M^+], 178 (100) [$M^+ - H_2O$], 160 (86) [$M^+ - 2H_2O$]. **6b**: m/z (%) = 196 (78), [M^+], 178 (91) [$M^+ - H_2O$], 160 (75) [$M^+ - 2H_2O$]. **6c**: m/z (%) = 196 (56), [M^+], 178 (94) [$M^+ - H_2O$], 160 (77) [$M^+ - 2H_2O$]. **6d**: m/z (%) = 196 (65), [M^+], 178 (99) [$M^+ - H_2O$], 160 (82) [$M^+ - 2H_2O$].

$C_{12}H_{20}O_2$ (196.3) Calcd. C 73.43 H 10.27
Found C 74.02 H 10.34 (**6a**)
C 73.26 H 9.98 (**6c**)
C 74.01 H 10.58 (**6d**)

Configuration: **6a–c** could be obtained by hydrogenation of pure *cis*-**4**; therefore, the hydroxy groups have *cis* configuration. **6d** was obtained by hydrogenation of pure *trans*-**4**; the hydroxy groups possess *trans* configuration.

1,2,3,4,5,8-Hexahydronaphthaline-1,8-dicarboxylic Acid (**8**): To a well-stirred mixture of 3 l of liquid ammonia, 60 ml of water, and 55.0 g (0.25 mol) of 7 18.3 g (2.64 mol) of lithium ribbon was added in small portions during 2.5 h. The blue suspension was stirred for 30 min and acidified with ammonium chloride. After addition of 60 ml of water the ammonia was allowed to evaporate at room temp. The residue was taken up with water, the filtrate was acidified with 6 N HCl, and the white precipitate was, after washing with water, recrystallised with dichloromethane/acetone yielding 41.0 g (74%) of **8**, m.p. 174°C (dec.). – IR (KBr): 3400 cm^{-1} (OH), 1710 (CO), 1660 (C=C). – ^{1}H NMR ([D$_6$]dimethyl sulfoxide): δ = 1.50–2.06 (m, 6H, CH_2), 2.55 (br. s, 2H, allylic CH_2), 3.00 (m, 1H, C*H*CO_2H), 3.66 (m, 1H, C*H*CO_2H), 5.76 (m, 2H, =CH), 12.20 (br. s, 2H, CO_2H). – ^{13}C NMR ([D$_6$]dimethyl sulfoxide): δ = 19.8, 26.7, 29.4, 31.5 (4 t, C-2,3,4,5), 42.9, 46.0 (2 d, C-1,8), 121.9, 131.2 (2 s, C-9,10), 123.2, 125.8 (2 d, C-6,7), 173.3, 175.6 (2 s, COOH). – MS (70 eV): m/z (%) = 204 (9) [$M^+ - H_2O$].

$C_{12}H_{14}O_4$ (222.2) Calcd. C 64.85 H 6.35 O 28.80
Found C 64.77 H 6.39 O 28.84

1,2,3,4,5,6,7,8-Octahydronaphthalene-1,8-dicarboxylic Acid (**9**): Hydrogenation of 35.0 g (158 mmol) of **8** in 250 ml of dry methanol with 1 g of platinum dioxide at room temp. yielded after recrystallisation from methanol/dichloromethane 32.0 g (91%) of **9**, m.p. 92°C (dec.). – IR (KBr): 3400 cm^{-1} (OH), 1705 (CO), 1660 (C=C). – ^{1}H NMR ([D$_6$]dimethyl sulfoxide): δ = 1.45–1.95 (m, 12H, CH_2), 2.95 (br. s, C*H*CO_2H). – ^{13}C NMR ([D$_6$]dimethyl sulfoxide): δ = 19.7, 26.8, 30.2 (3 t, C-2,3,4,5,6,7), 43.5 (d, C-1,8), 123.7, 133.7 (2 s, C-9,10), 175.9 (s, COOH). – MS (70 eV): m/z (%) = 206 (12) [$M^+ - H_2O$].

$C_{12}H_{16}O_4$ (224.3) Calcd. C 64.27 H 7.19 O 28.54
Found C 64.26 H 7.01 O 28.73

Dimethyl 1,2,3,4,5,6,7,8-Octahydronaphthalene-1,8-dicarboxylate (**10**): 30.0 g (134 mmol) of **9** were esterified by refluxing in 500 ml of dry methanol and 10 ml of concd. sulfuric acid for 12 h yielding 27.3 g (81%) of **10**, b.p. 122°C (0.013 mbar). – IR (film): 1730 cm^{-1} (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.46–1.91 (m, 12H, CH_2), 3.00 (br. s, 2H, $CHCO_2R$), 3.55 (s, 6H, CO_2CH_3. – ^{13}C NMR ($CDCl_3$): δ = 19.59, 26.61, 30.15 (3 t, C-2,3,4,5,6,7), 43.49 (d, C-1,8), 51.19 (q, CH_3), 122.18, 135.31 (2 s, C-9,10), 174.90 (s, CO_2H).

$C_{14}H_{20}O_4$ (252.3) Calcd. C 66.65 H 7.99 O 25.36
Found C 66.85 H 8.05 O 25.10

10-Hydroxytricyclo[7.2.1.0^{5,12}]dodec-9-en-11-one (**11**): To a boiling (–33°C) solution of 10.0 g (435 mmol) of sodium in 200 ml of dry ether and 100 ml of liquid ammonia 26.0 g (103 mmol) of **10** in 100 ml of dry ether was added during 2.5 h; stirring was continued for 30 min until the blue colour disappeared. 100 g of ammonium chloride and 100 ml of water were added to the yellow suspension. After evaporation of the ammonia at room temp. and addition of 300 ml of water the mixture was acidified with 3 N HCl and extracted with ether. The evaporation residue of the combined and dried ether phases yielded after recrystallisation 10.3 g (52%) of **11**, m.p. 145°C. – IR (KBr): 3340 cm^{-1} (OH), 1690 (CO), 1650 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.30–2.25 (m, 12H, CH_2), 2.45–2.95 (m, 3H, 1,5,9-H), 6.44 (br. s, 1H, C*H*OH). – ^{13}C NMR ($CDCl_3$): δ = 20.06, 20.70, 22.94, 23.87, 25.28, 30.16, (6 t, C-2,3,4,6,7,8), 32.86, 39.02, 42.57 (3 d, C-1,5,9), 145.80, 147.30 (2 s, C-9,10), 206.22 (s, C-11). – MS (70 eV): m/z (%) = 192 (100) [M^+], 174 (33) [$M^+ - H_2O$], 164 (95) [$M^+ - C_2H_4$].

$C_{12}H_{16}O_2$ (192.3) Calcd. C 74.97 H 8.37 O 16.64
Found C 74.95 H 8.19 O 16.86

Hydrogenation of **11** under the conditions described for the hydrogenation of **4** (6 h) gave **6b** (92%).

(5α,9α)-Tricyclo[7.2.1.0^{5,12}]dodec-1(12)-en-11-one (**12**): After refluxing 8.5 g (44 mmol) of **11** in 120 ml of acetic acid and 48 g of 48% hydroiodic acid for 1 h the cooled solution was poured into 600 ml of aqueous sodium hydroxide/sodium hydrogen sulfite. The combined ether extracts of the decolourised mixture were washed with aqueous sodium hydrogen sulfite and then with 1 N NaOH until the wash remined alkaline. The evaporation residue of the dried ether solution yielded after distillation at 110°C/0.03 mbar 6.9 g (88%) of **12**. – IR (film): 1695 cm^{-1} (CO), 1650 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 0.89–2.39 (m, 14H, CH_2), 2.50 (m, 2H, CH). – ^{13}C NMR ($CDCl_3$): δ = 19.74, 20.64, 24.16, 29.45, 33.30, 33.62 (6 t, C-2,3,4,6,7,8), 36.09, 38.65 (2 d, C-5,9), 41.59 (t, C-10), 135.59, 137.64 (2 s, C-1,12), 206.64 (s, C-11). – MS (70 eV): *m/z* (%) = 176 (100) [M$^+$], 148 (57) [M$^+$ – C_2H_4], 134 (92) [M$^+$ – CH_2CO].

$C_{12}H_{16}O$ (176.3) Calcd. C 81.76 H 9.15 O 9.08
Found C 81.71 H 9.11 O 9.18

The tosylhydrazone of **12** was prepared by warming a solution of 0.3 ml of 2 N HCl, 1.0 g (5.4 mmol) of tosylhydrazide, and 0.90 g (5.1 mmol) of **12** in 10 ml of methanol to 50°C yielding 1.49 g (85%) of (5α,9α)-tricyclo[7.2.1.0^{5,12}]dodec-1(12)-en-11-one tosylhydrazone, m.p. 174°C (methanol).

(1α,5α,9α,12β)-Tricyclo[7.2.1.0^{5,12}]dodecan-11-one (**13**): To a well-stirred solution of 1.0 g (145 mmol) of lithium in 200 ml of liquid ammonia were added 5.2 g (30 mmol) of **12** in 100 ml of dry ether and after 10 min an excess of ammonium chloride in order to decompose the remaining lithium and the lithium enolate. After evaporation of the ether at room temp. 100 ml of water was added and the aqueous layer extracted with ether. The combined, washed, and dried ether phases gave after distillation 3.3 g (62%) of **13**, b.p. 98°C/0.03 mbar. The distillation residue (1.5 g) was oxidized with an excess of pyridinium chlorochromate in dry dichloromethane. Distillation yielded 1.1 g of **13** (total yield 82%). – IR (film): 1745 cm^{-1} (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.45–2.40 (m). – ^{13}C NMR ($CDCl_3$): δ = 25.07, 25.60, 26.60, 30.91, 32.13, 33.13, 39.10 (7 t, C-2,3,4,6,7,8,10), 40.38, 44..34, 52.90, 54.36 (4 d, C-1,5,9,12), 217.00 (s, C-11). – MS (70 eV): *m/z* (%) = 178 (76) [M$^+$], 160 (26) [M$^+$ – H_2O], 149 (18) [M$^+$ – C_2H_5], 134 (100) [$C_{10}H_{14}$].

$C_{12}H_{18}O$ (176.3) Calcd. C 80.86 H 10.18 O 8.98
Found C 81.03 H 10.51 O 8.82

(1α,5α,9α,12β)-Tricyclo[7.2.1.0^{5,12}]dodecan-11-one Tosylhydrazone (**14**): 4.3 g (24 mmol) of **13** was converted to the tosylhydrazone as described for **12** yielding 7.6 g (91%) of **14**, m.p. 168°C (methanol). – ^{1}H NMR ($CDCl_3$): δ = 0.70–2.38 (m, 18H, CH, CH_2), 2.40 (s, 3H, CH_3), 7.23 (s, 1H, NH), 7.29 (d, *J* = 9 Hz, 2H, Ar-H), 7.82 (d, *J* = 9 Hz, 2H, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 21.52 (q, Ar-CH_3), 25.74, 25.93, 27.57, 31.01, 32.17, 32.48, 34.40 (7 t, C-2,3,4,6,7,8,10), 40.28, 40.36, 48.13, 56.08 (4 d, C-1,5,9,12), 127.95, 129.28 (2 d, C-Ar), 135.5, 143.64 (2 s, C-Ar), 167.10 (s, C-11).

(1α,5α,9α,12β)-Tricyclo[7.2.1.0^{5,12}]dodec-10-ene (Ufolene, **15**): To a solution of 14.0 g (43 mmol) of **14** in 300 ml of dry ether was added under nitrogen during 1 h 11.0 g (172 mmol) of *n*-butyllithium in 100 ml of ether. The mixture was stirred for 10 min until the evolution of nitrogen had ceased, then 200 ml of water was added. The aquous phase was extracted with ether. The combined, washed, and dried ether phases gave after distillation 3.1 g (45%) of **15**, b.p. 102°C/20 mbar. – IR (film): 3025 cm^{-1} (=C–H), 1620 (C=C), 700 (=C–H). – ^{1}H NMR ($CDCl_3$): δ = 0.45–2.0 (m, 8H, CH, CH_2), 5.87 (s, 1H, C=CH). – ^{13}C NMR ($CDCl_3$): δ = 26.65, 30.17, 33.40 (3 t, *J* = 30 Hz, C-2,3,4,6,7,8), 37.71 (d, *J* = 30 Hz, C-5), 48.05 (d, *J* = 50 Hz, C-9), 61.42 (d, *J* = 30 Hz, C-1,9). – MS (70 eV): *m/z* (%) = 162 (89) [M$^+$], 147 (8) [M$^+$ – CH_3], 133 (86) [M$^+$ – C_2H_5], 119 (100) [M$^+$ – C_3H_7], 105 (61) [M$^+$ – C_4H_9], 91 (93) [C_7H_7].

$C_{12}H_{18}$ (162.3) Calcd. C 88.82 H 11.18
Found C 98.15 H 11.02

CAS Registry Numbers

2a: 40745-44-6 / **3**: 480-72-8 / *trans*-**4**: 2963-87-3 / *cis*-**4**: 2963-86-2 / **5**: 16897-64-6 / **6**: 115650-91-4 / **6d**: 115730-40-0 / **7**: 102193-19-1 / **8**: 115650-92-5 / **9**: 115650-93-6 / **10**: 115650-94-7 / **11**: 115650-95-8 / **12**: 115650-96-9 / **12** (tosylhydrazone): 115677-31-1 / **13**: 115730-39-7 / **14**: 115650-97-0 / **15**: 115650-98-1 / acenaphthenequinone: 82-86-0

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[1] X-ray analysis of **6d** and of the tosylhydrazone of **12**.

[2] X-ray analysis of **14**.

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