85. Apparent Failure of the *Wharton* Rearrangement in a Tricyclo[7.1.1.0^{2,7}]undecane

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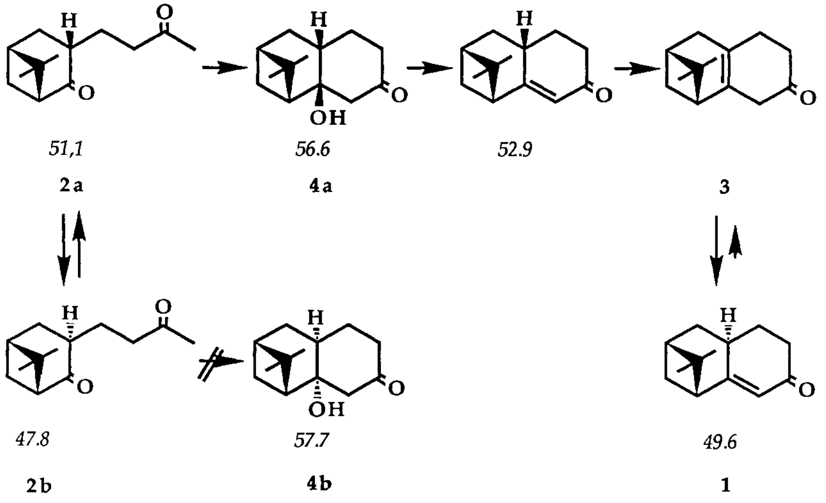
Dedicated to Dr. *G. Ohloff* on the occasion of his 65th birthday

(5.IV.89)

The *Wharton* rearrangement of 2,3-epoxytricyclo[7.1.1.0^{2,7}]undecan-3-one, a sterically hindered system, which should have led to an allyl alcohol with the OH group at a bridgehead, gave instead the allylically rearranged alcohol. The desired hydroxy compound was prepared by the *Barton* modification of the *Wharton* rearrangement: borohydride reduction to the epoxy alcohols, reaction with *N,N'*-thiocarbonylbisimidazole, and treatment with Bu_3SnH. The bridgehead alcohol (and other 2-oxygenated tricyclo[7.1.1.0^{2,7}]undecanes) readily rearranged under acidic or thermal conditions.

cis-10,10-Dimethyltricyclo[7.1.1.0^{2,7}]undec-2-en-4-one (**1**, Tricyclone¹)) was described 10 years ago [1], and the configuration verified [2]. The *Robinson* annulation leading to **1** was shown to occur *via* the *trans*-diketone **2a**, giving the *cis*-product **1** *via* the unconjugated ketone **3**. *Scheme 1* illustrates the situation, and we have calculated the MM2 energies for the compounds [3] as shown²). These values support the explanation we gave

Scheme 1



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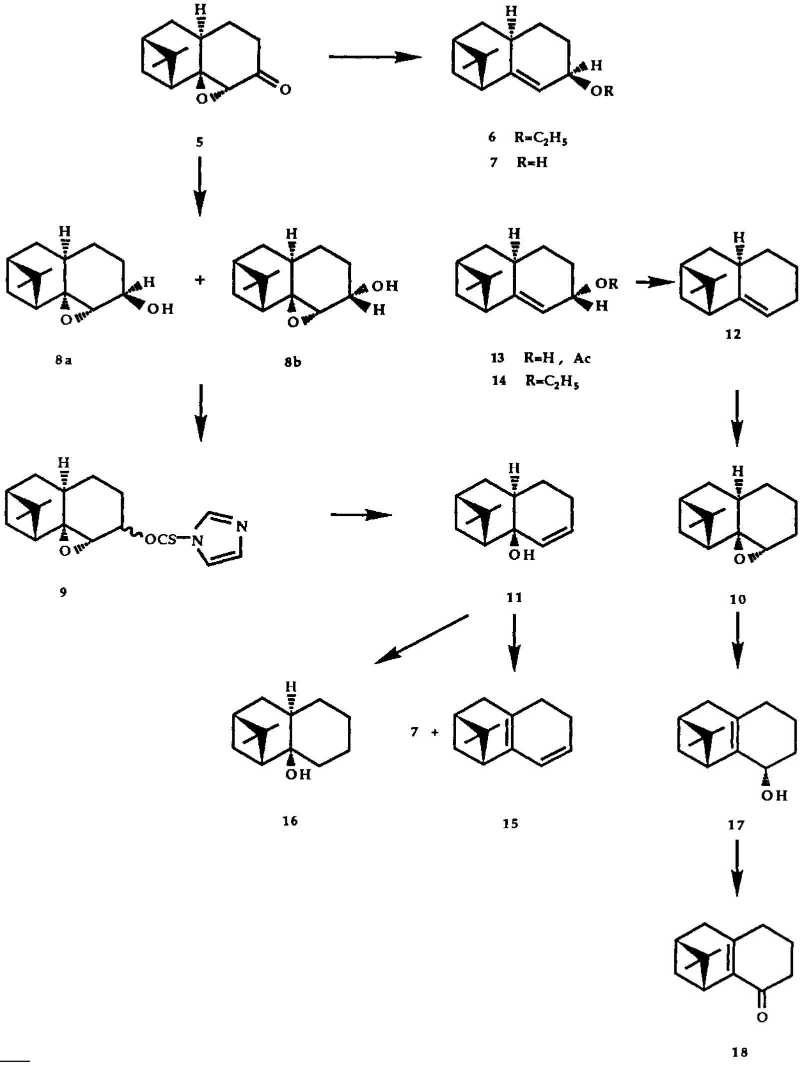
¹) Brand name of *Firmenich SA*.

²) The MM2 energies (kcal/mol) are given under each formula. We are aware that the *Still* programme [3] does not take conjugation of unsaturated ketones into account, but in the values quoted in *Scheme 1*, it is important to compare differences between stereoisomers only. We thank Dr. *B. Winter* for the energy calculations.

earlier [1]. The aldol condensation products **4a** and **4b** have never been observed, and we now report attempts to prepare tricyclo[7.1.1.0^{2,7}]undecanes having an angular OH group at C(2).

The epoxy ketone **5** *(Scheme 2)* was prepared from **1**, and treated with hydrazine hydrate in EtOH (*Wharton* conditions [4]). Gas chromatography showed that 11% of the product was unchanged starting material, and two new products had been formed. These were identified as 4β-ethoxy-10,10-dimethyl-7αH-tricyclo[7.1.1.0^{2,7}]undec-2-ene (**6**)[3] and the more polar crystalline 10,10-dimethyl-7-αH-tricyclo[7.1.1.0^{2,7}]undec-2-en-4β-ol (**7**).

Scheme 2



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[3] We use the convention α to mean on the opposite side of the gem-dimethyl group and β on the same side of the molecule as the gem-dimethyl group [2].

The alternative to the *Wharton* rearrangement proposed by *Barton et al.* [5] was carried out by first reducing the epoxy ketone **5** with $NaBH_4$ to the two corresponding epimeric alcohols **8a** and **8b**, in about equal porportions. Although these were readily separable on a silica-gel column, it turned out that this was not necessary, since in a control experiment, it was shown that both isomers gave the same result. Treatment of the alcohols with *N,N*-thiocarbonylbisimidazole yielded the thioimidazolides **9**, which were reduced with Bu_3SnH in the presence of azobis(isobutyronitrile). There was obtained in poor yield a *ca.* 4:1 ratio of the epoxide **10** and the desired 10,10-dimethyltricyclo[7.1.1.$0^{2,7}$]undec-3-en-2α-ol (**11**). The latter compound was not stable in the solvents normally used for the measurements of the NMR spectra, even the small amount of acid present being enough to cause allylic rearrangement ($\rightarrow$ **7**) and dehydration ($\rightarrow$ **15**). Both products tenaciously retained a sulfurous odour, and indeed catalytic reduction of **11** was only possible after primarily shaking with *Raney*-Ni to remove sulfur. The dihydro compound **16** also loses H_2O easily, for example, by gas chromatography.

To prepare a sample of the epoxide **10** free from sulfur, we decided to epoxidize the hydrocarbon **12**. This substance had already been obtained from the thioacetal of Tricyclone (**1**) [6], but this route too involves an unacceptable risk of sulfur contamination, while $LiAlH_4$ and $AlCl_3$ reduction of **1** would lead to a mixture of hydrocarbons (*cf.* [7]). We, therefore, reduced the acetate of 10,10-dimethyltricyclo[7.1.1.$0^{2,7}$]undec-2-en-4α-ol (**13**; made by metal hydride reduction of Tricyclone [2]) with Li in NH_3, and epoxidized the hydrocarbon **12** thus obtained.

The epoxide **10** is also thermally unstable, and decomposes to some extent on gas chromatography. Pyrolysis at 220° of this epoxide yielded a mixture, the main component of which was the alcohol **17**, obtained in better purity by treatment of **10** with Et_2NLi. This allyl alcohol **17** is readily oxidized by MnO_2 to the corresponding ketone **18**.

The configuration of all compounds containing an O-substituent at C(2) on the opposite side of the ring from the gem-dimethyl bridge is demonstrated by their ^{1}H-NMR spectra, in which the signal of the H_{syn}–C(11) is shifted markedly downfield to below 1.65 ppm. Without this O-atom, the signal of H–C(11) is generally above 1.60 ppm [2]. For comparison, the positions of the corresponding H–C(7) in the epoxides of β-pinene are at 1.43 ppm in the *cis*-isomer **19**, and 1.66 ppm in the *trans*-isomer **20** [8]. The configuration of the epoxy ketone **5** is also supported by the existence of a clear nuclear *Overhauser* effect between the *syn*-Me group and H–C(3) on the epoxide ring. The alcohol **7** obtained after the *Wharton* reaction of **5** was readily assigned the β-configuration, by comparison of its ^{1}H-NMR spectrum with that of the known α-isomer **13** (R = H) for which the structure was in no doubt [2]. In particular, the effect of the O-atom on the *syn*-Me group was to shift it from 0.63 to 0.67 ppm. The difference between the ethyl ethers **6** and **14** (the latter prepared from **13** (R = H)) was equally clear;

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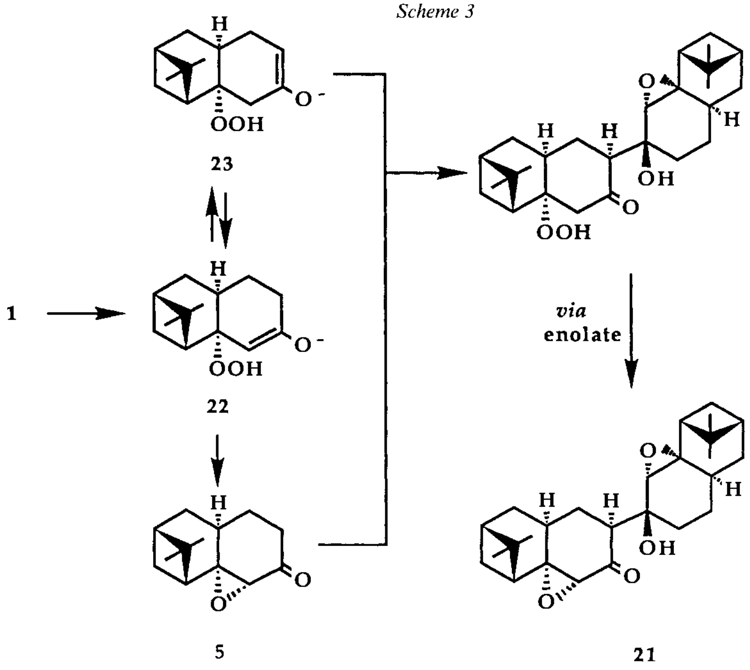
in addition to the effect of the O-atom on the *syn*-Me group (shifted from 0.59 ppm in **14** to 0.69 ppm in **6**), the effect on the bridgehead proton (H–C(7)) is also apparent, the signal shifting from 2.53 ppm in **14** to 2.40 in **6**.

Although the epoxy ketone **5** does not appear to be particularly unstable, other compounds having an angular O-substituent at C(2) clearly are, presumably because of steric strain. In the allyl alcohol **11**, dehydration competes with allyl rearrangement in the presence of traces of acid at room temperature, while basic conditions lead exclusively to allyl rearrangement. One might have expected some products from *Wagner-Meerwein* rearrangement in the presence of acid, but we did not detect any. The unusually low temperature needed for the pyrolysis of the epoxide **10** also attests to the steric instability.

We should like to take this opportunity to report an unusual product isolated during the preparation of the epoxide **5**. Isolation of **5** involved its solution in hexane, in which it dissolves readily, but crystals from the crude product remained. These crystals were soluble in Et_2O, and re-precipitation with hexane yielded pure material to which we ascribe structure **21** (*Scheme 3*), based on the high m.p. and the NMR spectra. The NMR spectra show clearly the presence of two protons on oxiranes, one C=O group, and a tertiary OH group. The elemental analysis shows the same proportion of C and H as **5**, and the ^{13}C-NMR signals corresponding to the pinane part of the skeleton are doubled. There is only one stereoisomer visible, and there is spectral evidence for an H-bond.

Treatment of **5** with base does not lead to the dimer **21**, so there is some factor other than that associated with a simple aldol condensation that must be considered. One possibility[4]) is that the hydroperoxy enolate **22**, presumably an intermediate in the

Scheme 3



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[4]) We are indebted to Dr. *K. H. Schulte-Elte* for this suggestion.

epoxidation reaction, is thermodynamically less stable than the isomer **23**, and has sufficient time to be converted to the latter before losing an OH^- ion to form the epoxide. The enolate **23** can then react in an aldol reaction with the epoxide **5** before formation of the epoxide **21**. The alternative sequence of events, with enolate **23** reacting with Tricyclone (**1**), followed by epoxidation of the product, is another possibility. The configuration we show corresponds to attack of the enolate on a C=O group from the side of the molecule opposite to the *gem*-dimethyl group, but other configurations are also possible.

Experimental Part

General. Optical rotations are measured in $CDCl_3$ (*c* 1%). Prep. GLC was carried out on a *Carlo-Erba* type *GT* chromatograph using He as a carrier gas. NMR spectra: in $CDCl_3$ on a *Bruker WH-360* instrument. Chemical shifts are given in ppm downfield from TMS (=0 ppm), coupling constants *J* in Hz. Where attributions of ^{1}H- and ^{13}C-NMR spectra are given, they were generally checked by COSY and ^{1}H, ^{13}C-correlations measurements. Mass spectra: *Finnigan 1020* instrument; in *m/z* (% most important fragment), generally the ten most important fragments are given. Microanalyses were done by Drs *H.* and *K. Eder*, Institut de Chimie Pharmaceutique (Service de Microchimie), University of Geneva.

2α,3α-Epoxy-10,10-dimethyl-7αH-tricyclo[7.1.1.0^{2,7}*]undecan-4-one* (**5**). To Tricyclone [1] (120 g, 0.62 mol) was added, dropwise with stirring, a soln. of H_2O_2 (182 ml, 35%) in MeOH (600 ml), while maintaining the temp. between 5 and 10°. This was followed by the dropwise addition of NaOH (6N, 52 ml, 0.31 mol) at such a rate that the temp. was maintained at *ca.* 15°. The mixture was then stirred at 20° (thermostatted), and poured into 700 ml of H_2O. The product was extracted with Et_2O (3 ×) and AcOEt (once). The combined org. extracts were washed, and, after adding $(MeO)_3P$ (10 ml) to remove peroxides, the soln. was concentrated at r.t. to yield 115.4 g of crude crystalline material. Most of this material dissolved in warm hexane, which on cooling gave pure **5**. M.p. 86–88°. $[\alpha]_D^{20} = +36.2$. ^{1}H-NMR: 0.85, 1.25 (2 *s*, 2 CH_3); 1.44 (*dd, J* = 13, 7.5, H_β–C(8)); 1.52 (*dd, J* = 4.5, 4.5, H–C(1)); 1.71 (*d, J* = 10, H_{syn}–C(11)); 2.78 (*dd, J* = 14, 5, H_β–C(5)); 2.98 (*s*, H–C(3)). ^{13}C-NMR: 20.9 (*q*); 25.5 (*t*, C(11)); 25.9 (*q*); 29.1 (*d*, C(7)); 30.8 (*t*, C(8)); 32.7 (*t*, C(6)); 35.5 (*t*, C(5)); 40.5 (*d*, C(9)); 40.5 (*s*, C(10)); 49.4 (*d*, C(1)); 61.8 (*d*, C(3)); 74.3 (C(2)); 208.5 (C(4)). MS: 79 (100), 91 (90), 41 (85), 69 (73), 55 (68), 77 (55), 83 (55), 135 (55), 107 (52), 117 (50), ... 191 (5), 206 (3, $M^{+\cdot}$). Anal. calc. for $C_{13}H_{18}O_2$ (206.27): C 75.69, H 8.81; found: C 75.21, H 8.80.

The crystals remaining undissolved in hexane were dissolved in Et_2O and re-precipitated with hexane, when they had m.p. 188–190°; $[\alpha]_D^{20} = -16.2$. This appeared to be *2α,3α-epoxy-5β-(2α,3α-epoxy-4β-hydroxy-10,10-dimethyl-7αH-tricyclo[7.1.1.0*^{2,7}*]undec-4-yl)-10,10-dimethyl-7αH-tricyclo[7.1.1.0*^{2,7}*]undecan-4-one* (**21**). ^{1}H-NMR: 0.84, 0.92, 1.22, 1.25 (4 *s*, 4 CH_3); 1.63, 1.68 (2 *d*, H_{syn} of cyclobutane rings); 2.99, 3.07 (2 *s*, oxirane H); 3.09 (*dd, J* = 4, 13, CHCO); 3.73 (*s*, 1 H, disappears on adding D_2O; OH···O=C). ^{13}C-NMR: 24.2 (*t*); 25.5, 25.6 (2 *t*, C(11), C(11′)); 28.8, 29.5 (2 *d*, C(7), C(7′)); 30.7 (*t*, C(8), C(8′)); 31.3 (*t*); 35.2 (*t*); 40.6, 41.1 (2 *d*, C(9), C(9′)); 40.8 (2(?) *s*, CH_3); 49.3, 49.9 (2 *d*, C(1), C(1′)); 51.0 (*d*, C(5)); 61.3, 63.5 (2 *d*, C(3), C(3′)); 66.1 (*s*, C(4′)); 71.8 (2 *s*, C(2), C(2′)); 213.2 (*s*, C=O). MS (by direct probe): 69 (100), 91 (72), 79 (65), 55 (60), 83 and 41 (53), 107 (50), ... 189 (15), 191 (10), 206 (3), 412 (trace, $M^{+\cdot}$). Anal. calc. for $C_{26}H_{36}O_4$ (412.54): C 75.69, H 8.81; found: C 75.71, H 8.84.

Wharton *Reaction of* **5**. A soln. of **5** (9 g) in EtOH (150 ml) was stirred, while hydrazine hydrate (2.5 ml) was added dropwise. After stirring overnight, the mixture was carefully neutralized to pH 7 with a few drops of 10% H_2SO_4. GC showed, in addition to 11% of **5**, two new products (respectively 40 and 43% of the total). Chromatography on silica gel enabled these to be separated, but only with some decomposition, and they were better isolated by prep. GLC. The first, less polar substance was *4β-ethoxy-10,10-dimethyl-7αH-tricyclo[7.1.1.0*^{2,7}*]undec-2-ene* (**6**). ^{1}H-NMR: 0.69, 1.24 (2*s*, CH_3); 1.18 (*t*, CH_3CH_2); 1.43 (*d* + further coupling, *J* = 11, H_β–C(8)); 1.57 (*d, J* = 10, H_{syn}–C(11)); 2.38 (*dd, J* = 4.5, 4.5, H–C(1)); 3.51 (*q*, CH_2O); 3.77 (*dd, J* = 1.2, 1.2, H–C(4)); 5.38 (br. *s*, H–C(3)). ^{13}C-NMR: 15.9 (*q*); 21.6 (*q*); 24.8 (*t*, C(6)); 26.2 (*t*, C(11)); 26.5 (*q*); 29.3 (*t*, C(5)); 30.8 (*t*, C(8)); 31.2 (*d*, C(7)); 41.1 (*d*, C(9)); 42.4 (*s*, C(10)); 50.8 (*d*, C(1)); 62.9 (*t*, CH_3CH_2); 70.5 (*d*, C(4)); 118.5 (*d*, C(3)); 149.7 (*s*, C(2)). MS: 91 (100), 41 (65), 105 (60), 131 (45), 79 (43), 69 (38), 77 (37), 95 (35), ... 150 (25), 174 (13), 205 (8), 220 (15, $M^{+\cdot}$).

The more polar substance eluted later from either polar or apolar GLC columns was *10,10-dimethyl-7αH-tricyclo[7.1.1.0*^{2,7}*]undec-2-en-4β-ol* (**7**). Recrystallized from cyclohexane, this had m.p. 85–86°. $[\alpha]_D^{20} = +21.5$. ^{1}H-NMR: 0.67, 1.27 (2 *s*, CH_3); 1.57 (*d, J* = 10, H_{syn}–C(11)); 4.14 (*dd, J* ≈ 2.5, 2.5, H–C(4)); 5.38 (diffuse *dd, J* ≈ 1.5, 1.5, H–C(3)). ^{13}C-NMR: 21.6 (*q*); 24.1 (*t*, C(6)); 26.3 (*t*, C(11)); 26.4 (*q*); 30.8 (*t*, C(8)); 31.1 (*d*, C(7)); 32.0 (*t*, C(5)); 41.0 (*d* C(9)); 50.6 (*d*, C(1)); 64.1 (*d*, C(4)); 120.4 (*d*, C(3)); 150.1 (*s*, C(2)). MS: 96 (100), 109 (75), 91 (68), 131 (68), 95 (55), 41 (40), ... 174 (18), 177 (3), 192 (4, $M^{+\cdot}$).

4α-Ethoxy-10,10-dimethyl-7αH-tricyclo[7.1.1.0^{2,7}]undec-2-ene (**14**). This was prepared from the alcohol **13** (R=H; 1 g) [2], by treating it with 1 equiv. of NaH in THF followed by EtI. After 2 h at reflux, the mixture was poured into ice-water, the product isolated in pentane, and the material purified by prep. GLC on *Carbowax*. ^{1}H-NMR: 0.59, 1.19 (2 *s*, CH_3); 1.18 (*t*, CH_3CH_2); 1.47 (*m*, H_{α}–C(5)); 1.53 (*d*, $J = 10$, H_{syn}–C(11)); 1.82 (*m*, H_{α}–C(6)); 1.93 (*m*, H–C(9)); 2.17 superimposed on 2.20 (2 *m*, H_{β}–C(5), H_{anti}–C(11)); 2.35 (*dd*, $J = 3, 3$, H–C(1)); 2.53 (*m*, H–C(7)); 3.51 (*dq*, CH_3CH_2; the different magnetic environment for the 2 protons of the CH_2 group as compared with the same signal in the NMR of **6** is also consistent with the axial orientation of C_2H_5O in **14**); 4.04 (*m*, H–C(4)); 5.24 (br. *s*, H–C(3)). ^{13}C-NMR: 15.8 (*q*); 21.6 (*q*); 25.9 (*t*, C(11)); 26.4 (*q*); 28.8 (*t*, C(6)); 30.4 (*t*, C(5)); 30.7 (*d*, C(7)); 31.0 (*t*, C(8)); 41.1 (*d*, C(9)); 42.5 (*s*, C(10)); 50.5 (*d*, C(1)); 62.9 (*t*, CH_2O); 75.3 (*d*, C(4)); 119.9 (*d*, C(3)). MS: 91 (100), 105 (75), 131 (67), 150 (62), 95 (60), 69 (52), 79 and 123 (45), 77 (48), 67 (45), ... 174 and 177 (15), 205 (8), 220 (30, $M^{+\cdot}$).

2α,3α-Epoxy-10,10-dimethyl-7αH-tricyclo[7.1.1.0^{2,7}]undecan-4-ols (**8**). A mixture of **5** (10 g) and $NaBH_4$ (0.91 g) in H_2O (50 ml) was stirred while MeOH (50 ml) was added slowly, maintaining the temp. at 30° by cooling. After 1 h, the soln. was homogeneous, and the products were extracted into Et_2O. The Et_2O soln. was washed (H_2O), dried, and concentrated to yield 10.8 g of a mixture of 2 products (by TLC) which could be separated by chromatography on silica gel. The less polar substance was the 4α-hydroxy-epoxide **8b**. M.p. 84–85° (cyclohexane). ^{1}H-NMR: 0.95, 1.24 (2 *s*, CH_3); 1.68 (*d*, $J = 10$, H_{syn}–C(11)); 2.26 (*m*, H–C(7)); 2.89 (*s*, H–C(3)); 4.36 (br. *s*, H_{β}–C(4)). MS: 41 (100), 91 (97), 55 (70), 79 (68), 77 (65), 39 and 43 (60), 83 (53); 67 and 93 (50), ... 147 (20), 151 (16), 190 (2), 208 (trace, $M^{+\cdot}$).

The *O*-thiocarbonylimidazolide of **8b** (*O-(2α,3α-epoxy-10,10-dimethyl-7α* H*-tricyclo[7.1.1.1^{2,7}]undec-4-yl) imidazole-1-thiocarboxylate*; **9**) was obtained by heating with 2 equiv. of *N,N'*-thiocarbonylbisimidazole in dry CH_2Cl_2 for 1.5 h [5]. After washing (H_2O, 2% H_2SO_4, H_2O, $NaHCO_3$ 5%, H_2O to pH 7), drying and concentrating, the product was purified by prep. TLC *(Chromatotron)*. ^{1}H-NMR: 0.97, 1.26 (2 *s*, CH_3); 1.72 (*d*, $J = 10$, H_{syn}–C(11)); 2.31 (*m*, H–C(7)); 3.11 (*s*, H–C(3)); 6.12 (*d*, $J = 1.5$, H–C(4)); 7.05, 7.62, 8.32 (3 *s*, imidazole H).

The second, more polar substance was the 4β-hydroxy-epoxide **8a**. M.p. 89–90° (cyclohexane). ^{1}H-NMR: 0.83, 1.24 (2 *s*, CH_3); 1.51 (*dd*, $J = 5, 5$, H–C(1)); 1.66 (*d*, $J = 10$, H_{syn}–C(11)); 2.25 (*m*, H–C(7)); 3.06 (*s*, H–C(3)); 3.96 (*dd*, $J = 4, 10$, H–C(4)). MS: 41 (100), 91 (90), 55 and 77 (70), 79 (68), 39 (63), 43 and 83 (60), 93 (55), ... 147 (20), 151 (10), 193 (3), 190 (2), 208 (trace, $M^{+\cdot}$).

The *O*-thiocarbonylimidazolide of **8a** was prepared as for the other isomer, and had ^{1}H-NMR: 0.90, 1.25 (2 *s*, CH_3); 1.53 (*dd*, $J = 5, 5$, H–C(1)); 1.69 (*d*, $J = 10$, H_{syn}–C(11)); 2.30 (*m*, H–C(7)); 3.27 (*s*, H–C(3)); 5.91 (*dd* + further coupling, $J = 4, 10$, H–C(4)); 7.04, 7.66, 8.39 (3 *s*, imidazole H).

10,10-Dimethyl-7α-tricyclo[7.1.1.0^{2,7}]undec-3-en-1α-ol (**11**). After a preliminary experiment had shown that both isomers of **8** behaved in the same way, work was carried out on the mixture. The *O*-thiocarbonylimidazolides **9** were prepared as described in the foregoing experiment, and, without chromatographic separation, the crude material was treated as follows. The *O*-thiocarbonylimidazolides **9** (12 g) in benzene (40 ml) were stirred at 85° while Bu_3SnH (16.4 g) and azobis(isobutyronitrile) (50 mg) in benzene (90 ml) were added over 30 min. After cooling, the mixture was poured into ice-water. The product was extracted into toluene, and the combined org. phases were washed with H_2O, dried, and concentrated to give 21 g of crude material, which was clearly still very impure. Flash chromatography (silica gel, cyclohexane/AcOEt 9:1) yielded, first, 1.52 g of *2α,3α-epoxy-10,10-dimethyl-7αH-tricyclo[7.1.1.0^{2,7}]undecane* (**10**), which was purified by re-chromatography and bulb-to-bulb distillation. $[\alpha]_D^{20} = -29.4$. ^{1}H-NMR: 0.85, 1.23 (2 *s*, CH_3); 1.48 (*dd*, $J = 5, 5$, H–C(1)); 1.68 (*d*, $J = 10$, H_{syn}–C(11)); 2.21 (*m*, H–C(7)); 2,92 (*s*, H–C(3)). ^{13}C-NMR: 18.2 (*t*, C(5)); 21.3 (*q*); 25.4 (*t*, C(11)); 25.9 (*t*, C(4)); 26.3 (*q*); 29.5 (*d*, C(7)); 29.6 (*t*, C(6)); 31.7 (*t*, C(8)); 40.4 (*s*, C(10)); 41.0 (*d*, C(9)); 50.1 (*d*, C(1)); 60.0 (*d*, C(3)); 64.4 (*s*, C(2)). MS: 79 (100), 55 (93), 83 and 91 (80), 107 (75), 93 (60), 67, 81, and 149 (50), 77 (48), ... 177 (18), 192 (5, $M^{+\cdot}$).

There were later eluted 0.51 g of white crystals, m. p. 83–84° (cyclohexane), identified as **11** by ^{1}H-NMR: 0.73, 1.23 (2 *s*, CH_3); 1.82 (*d*, $J = 10$, H_{syn}–C(11)); 5.62 (*d*, $J = 10$, H–C(3)); 5.86 (*ddd*, $J = 4, 4, 10$, H–C(4)). ^{13}C-NMR ((D_6)acetone): 21.7 (*t*); 21.7 (*q*); 24.1 (*t*); 26.1 (*t*); 29.1 (*t*); 29.1 (*q*); 35.9 (*d*, C(7)); 40.4 (*s*, C(10)); 41.5 (*d*, C(9)); 53.7 (*d*, C(1)); 71.3 (*s*, C(2)); 128.5 (*d*, C(4)); 136.5 (*d*, C(3)). Measured immediately in $CDCl_3$, the ^{13}C-NMR spectrum exhibited signals at *ca.* the same position (with some difficulty in identifying the singulets), but after 24 h in soln., there began to appear signals corresponding to *10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2(7),3-diene* (**15**), notably *s* at 126.3 and 137.2, and *d* at 128.0 and 122.3, together with the signals associated with **7**. Finally the signals of **11** disappeared completely. An ^{1}H-NMR spectrum measured in $CDCl_3$ on a sample that had partly decomposed exhibited the signals of **7** and **11**, together with the following signals attributed to **15**: 0.77, 1.28 (2 *s*, CH_3); 2.19, 2.27 (each br. *t*, 2H–C(5), and 2H–C(6)); 5.57 (*m*, H–C(4)); 5.68 (*d*, $J = 8$, H–C(3)). MS of **11**: 96 (100), 109 (55), 95 (40), 91 (38), 131 (35), 67 (26), 55 (22), 79 (22), 41 (20), 77 (20), ... 174 (7), 177 (1), 192 (2, $M^{+\cdot}$).

10,10-Dimethyl-7αH-tricyclo[7.1.1.0^{2,7}]undecan-2α-ol (**16**). The alcohol **11** (0.9 g) was shaken in alcohol repeatedly with fresh *Raney*-Ni (100 mg), until there was no more odour of sulfur. The *Raney*-Ni was then replaced with 0.2 g of fresh catalyst, and the mixture hydrogenated in a *Parr* hydrogenator at 62 psi for 48 h. GLC of the product showed that the hydrogenation was still only partly complete, but the newly formed peak was collected, and had the following ^{1}H-NMR: 0.91, 1.23 (2 *s*, CH_3); 1.615 (*d*, $J = 10$, H_{syn}–C(11)); 2.16 (5 lines, H–C(7)). MS: 82 (100), 41 (74), 91 (72), 55 (65), 133 (65), 98 (62), 111 (50), ... 176 (10), 179 (15), 194 (3, $M^{+\cdot}$).

10,10-Dimethyl-7αH-tricyclo[7.1.1.0^{2,7}]undec-2-ene (**12**; *cf.* [6]). A soln. of 10,10-dimethyl-7αH-tricyclo-[7.1.1.0^{2,7}]undec-2-en-3α-yl acetate (24 g) in $EtNH_2$ (125 ml) was stirred, while small pieces of Li were added. In all, 10 g of Li was added over 15 min. The mixture was stirred overnight, then a large excess of NH_4Cl was added (carefully at first), followed by H_2O (500 ml). The product was isolated in cyclohexane and, after washing and concentrating the solvent, was purified by filtration through a short column of silica gel in hexane. Yield 9.8 g (53%). ^{13}C-NMR: 21.6 (*q*); 24.6 (*t*); 25.0 (*t*); 26.3 (*t*); 26.5 (*q*); 29.8 (*t*); 30.4 (*d*, C(7)); 31.3 (*t*); 41.3 (*d*, C(9)); 42.5 (*s*, C(10)); 50.8 (*d*, C(1)); 143.8 (*s*, C(2)); 188.1 (*d*, C(3)).

2α,3α-Epoxy-10,10-dimethyl-7αH-tricyclo[7.1.1.0^{2,7}]undecane (**10**). A mixture of **12** (1 g) and AcONa (0.4 g) in CH_2Cl_2 (5 ml) was stirred at 0°, while CH_3COOOH (40%, 0.8 ml) was added dropwise. After stirring for 30 min at 0°, the soln. was allowed to come to r. t., then stirred for 24 h. The usual workup (washing to neutrality, drying, and concentrating) gave 48% (by GLC) of **10**. When Na_2CO_3 was used in place of AcONa as the buffer, the yield rose to 85%. NMR and MS: identical with those of the sample mentioned above.

10,10-Dimethyltricyclo[7.1.1.0^{2,7}]undec-2(7)-en-3α-ol (**17**). *A*) The epoxide **10** was heated in Ar at 22° for 1 h, then bulb-to-bulb-distilled to yield 0.4 g of material still containing *ca.* 15% of **10**. The major product (*ca.* 75%) was **17**, which was isolated for spectra by prep. GLC on *Carbowax*.

B) Et_2NLi prepared from Et_2NH (5.8 ml) and BuLi (15% in hexane, 38 ml) in dry THF (30 ml) was stirred at 20°, while **10** (10 g) was added dropwise. The mixture was stirred for 20 h, then poured onto ice and extraced with Et_2O. After washing (H_2O, H_2SO_4, $NaHCO_3$, H_2O), drying, and concentrating, there was obtained 8.0 g (80%) of nearly pure **17**, which was purified by bulb-to-bulb distillation and chromatography over silica gel. $[\alpha]_D^{20} = -76.6$. ^{1}H-NMR: 0.75, 1.29 (2 *s*, CH_3); 1.18 (*d*, $J = 10$, H_{syn}–C(11)); 2.24 (*dd*, $J = 4.5, 4.5$, H–C(1)); 3.86 (br. *s*, H–C(3)). MS: 131 (100), 41 (28), 91 (25), 43 (18), 130 and 39 (15), 105 (14), ... 149 (8), 159 (5), 174 and 177 (3), 192 (8, $M^{+\cdot}$).

10,10-Dimethyltricyclo[7.1.1.0^{2,7}]undec-2(7)-en-3-one (**18**). A mixture of **17** (1.5 g) and MnO_2 (15 g, activated at 120° for 1 h) in dry Et_2O (150 ml) was shaken for 1 h. After filtering through *Celite*, the soln. was concentrated to yield 1.4 g of material. This was distilled in a bulb tube, and the product (1.1 g) then consisted of 10% of **17** and 78% of **18**. The latter was purified by prep. GLC on *Carbowax*. ^{1}H-NMR: 0.70, 1.32 (2 *s*, CH_3); 1.02 (*d*, H_{syn}–C(11)); 2.01 (5 lines, 2 H–C(5)); 2.12 (*m*, H–C(9)); 2.29 (*dd*, 2 H–C(6)); 2.34–2.50 (*m*, 5 H); 2.95 (*dd*, $J = 4.5, 4.5$, H–C(1)). ^{13}C-NMR: 20,5 (*q*); 22.9 (*t*); 25.9 (*q*); 29.2 (*t*); 37.38 (*t*, 2 C); 37.44 (*d*); 38.7 (*s*); 40.4 (*d*); 141.9 (*s*); 155.4 (*s*); 196.6 (*s*). MS: 91 (100), 147 (93), 146 (31), 41 (25), 105 (25), 129 (14), 119 (23), 77 (20), ... 175 (10), 190 (7, $M^{+\cdot}$).

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