14. The Configuration of Tricyclo[7.1.1.$0^{2,7}$]undecanes and the Stereochemistry of the Reduction of Tricyclone

by **Alan F. Thomas, Walter Thommen** and **Josef Becker**

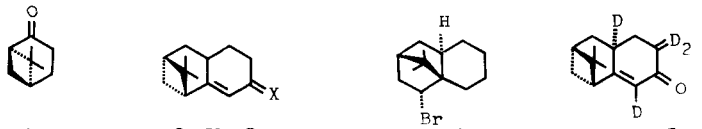
Firmenich SA, Research Laboratories, CH-1211 Geneva 8

(5.XI.80)

Summary

A full discussion of the configuration of tricyclo[7.1.1.$0^{2,7}$]undecanes related to *cis*-10,10-dimethyltricyclo[7.1.1.$0^{2,7}$]undec-2-en-4-one (**2**), the *Robinson* annelation product from norpinone **1** and 3-buten-2-one is given, based on 360-MHz-NMR. spectra. Nuclear *Overhauser* effects confirm the *cis* configuration of **2**, and show that the saturated ketone **10**, obtained by catalytic hydrogenation, is also all-*cis* with the cyclohexanone ring in the boat conformation. The parent hydrocarbon, *cis*-10,10-dimethyltricyclo[7.1.1.$0^{2,7}$]undecane is compared with one of the corresponding *trans* isomers prepared from pinocarvone (**14**). The stereochemistry of metal hydride reduction and *Grignard* reaction of **2** is examined.

Earlier work has suggested that 'Tricyclone'[1]), the compound formed by *Robinson* annulation of 3-buten-2-one to the norpinone **1** should be ascribed the *cis* configuration **2** [1]. This attribution is supported by the observations of *Barthélémy & Bessière* [2] [3] who showed that under non-solvating conditions, the ions formed by addition of HBr to β-pinenes rearrange by migration of the gem-dimethyl bridge (to bornanes) in the case of *cis*-substitution, and of the methylene bridge (to fenchanes) in the case of *trans*-substitution. The hydrocarbon **3** derived from **2** rearranges to the bornane **4** under these conditions.



1 **2** X=O; **3** X=H_2 **4** **5**

Nevertheless, direct spectral evidence for the configuration of **2** was lacking, and we now present a full discussion of the NMR. spectra of this and related substances, and describe the stereochemistry of various reductions of **2**.

Base-catalyzed deuterium exchange [4] of **2** yielded mainly the tetradeuteriated compound **5**, and it was possible to analyze the 360-MHz-^{1}H-NMR. spectrum in detail (see *Table 1* for a list of the chemical shifts of **2**, **5**, and other related

[1]) Brand name of *Firmenich SA*.

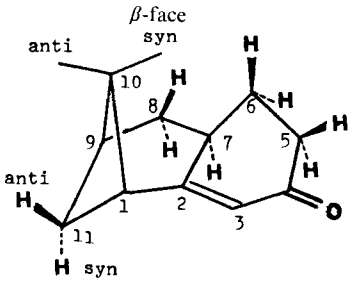
0018-019X/81/1/0161-10$01.00/0

Table 1. *^{1}H-NMR. signals of tricyclo[7.1.1.0^{2,7}]undecenes*

Substance	H–C(1)	H_α–C(5)	H_β–C(5)	H_α–C(6)	H_β–C(6)	H–C(7)	H_α–C(8)	H_β–C(8)	H–C(9)	H(*syn*)–C(11)	H(*anti*)–C(11)	*syn*-Me	*anti*-Me	Other
2	2.61	2.34	2.50	2.05	1.81	2.81	2.19	1.53	2.10	1.58	2.38	0.63	1.30	C(3) 5.73
5	2.62	–	–	2.08	1.79	–	other protons as for **2**							
6	3.03	2.31	2.55	2.04	1.75	2.82	2.18	1.51	2.07	1.58	2.37	0.69	1.35	Me 1.68
7[a])	2.61	2.33	–	(2.07)	(1.51)	2.90	(2.15)	(1.52)	2.07	1.59	2.36	0.68	1.30	Me 1.13 C(3) 5.72
8	3.00	2.30	–	2.04	(1.51)	2.88	2.16	(1.52)	2.07	1.59	2.36	0.67	1.35	Me 1.68, 1.17
9	3.02	–	2.57	1.84	1.94	2.99	2.15	1.53	2.09	1.61	2.37	0.68	1.36	Me 1.67, 1.17
20	2.36	1.43	2.21	1.85	1.43	2.55	(1.98)	(1.41)	(1.98)	1.58	2.26	0.63	1.24	C(3) 5.21 C(4) 4.39
23	2.38	1.59	2.22	(1.87)	(1.48)	2.59	(1.98)	(1.41)	1.98	1.58	2.26	0.61	1.23	C(3) 5.17 C(4) 5.49
21	2.32	1.72	2.00	1.85	1.43	2.53	(1.98)	1.38	(1.97)	1.56	2.24	0.62	1.23	Me 1.30 C(3) 5.11
22	2.33	1.58	1.91	1.46	?	2.40	?	(1.40)	1.99	1.56	2.26	0.66	1.23	Me 1.28 C(3) 5.22
		C(2)	C(3)											
18	1.78	(2.83)	1.78		5.93	–	2.57	2.83	2.01	1.08	2.27	0.91	1.29	C(4)α 2.50 C(4)β 2.38

[a]) The 5α-methyl isomer was present as impurity, having C(3)H 5.67, C(5)βH 2.54, C(5)Me 1.19, Me(*anti*) 1.31. Value in parantheses mean that the exact position could not be located of interfering signals. All measurements refer to those made in $CDCl_3$.

compounds described in this paper). Based on the chemical shifts thus established, nuclear *Overhauser* effect (NOE) measurements enabled the following steric relationships to be made. Irradiation of H(*syn*)–C(11) produced a NOE on H(*anti*)–C(11), H–C(1), H–C(9) and particularly H–C(7), thereby proving that the latter proton was on the same side (the *β*-face, formula **A**) of the molecule as *H(syn)*–C(11). Irradiation of the *anti*-methyl group on C(10) produced a NOE on H–C(1), H(*anti*)–C(11), and H–C(9), while irradiation of the other (*syn*) methyl group produced a NOE on H–C(1), H–C(9), H_β–C(6) and H_β–C(8), but not on H–C(7). The configuration of **2** is thus conclusively established.



A

Decoupling experiments revealed the coupling constants of **2** as shown in *Table 2*. Concerning the cyclobutane part of the system, these are generally in accord with previous studies [5] [6], confirming in particular, that the coupling constant between the protons at C(7,8) is greater when these are *cis* than when they are *trans* [7]. The use of coupling constants as well as consideration of the influence of various substituents on the chemical shift of the gem-dimethyl groups [8], has led to the establishment of preferred conformations for simple pinane derivatives [7–12]. Application of the modified *Karplus* equations [9]

$$J = 9.3\cos^2\varphi + \cos\varphi \text{ (for dihedral angles } < 90°)$$
$$J = 12.7\cos^2\varphi + \cos\varphi \text{ (for dihedral angles } 90\text{–}180°)$$

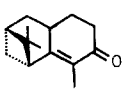
leads to a dihedral angle of 5–10° between H–C(7) and the *cis* H_α–C(8), with at least 135° for the angle with the *trans* proton. This corresponds to a conformation **A**

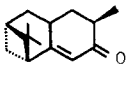
Table 2. *Coupling constants (J, Hz) for ketones* **2** *and* **9** (the sign of the coupling is ignored)

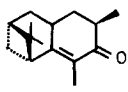
Protons on C-atoms no.	*J* **2**	**9**	Protons on C-atoms no.	*J* **2**	**9**
1,11	5	5	6β,7	13	11
1,9	4	5	6α,7	3	5
3,7 (**2**); Me,7 (**9**)	7	2.5	7,8β	8	8
5α,5β	18	–	7,8α	10	5
5α,6β	14	–	8α,8β	13	12
5β,6β	4	5	8β,9	*ca.* 1	<0.5
5β,6α	3	1.5	8α,9	4	5
6α,6β	13	13	9,11(*anti*)	5	5
			11(*syn*),11(*anti*)	10	9.5

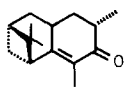
having C(7) a little below the plane of the C(1,2,8,9)-atoms, and with C(2,3,4,5) practically coplanar.

Some homologues of 'Tricyclone' (**2**) were prepared to investigate the effect of methyl groups on the NMR. spectrum. We have already [1] questioned the statement of *Brown et al.* [13] that 3,10,10-trimethyltricyclo[7.1.1.$0^{2,7}$]-undec-2-en-4-one (**6**) could not be made by the method we have used for **2**; indeed, it was readily made from norpinone enamine and 1-penten-3-one. A mixture of the two isomers of 5,10,10-trimethyltricyclo[7.1.1.$0^{2,7}$]undec-2-en-4-one, mostly the 5β-methyl isomer **7**, was obtained by methylation of the enolate of 'Tricyclone' (**2**) with methyl iodide. The two 3,5,10,10-tetramethyltricyclo[7.1.1.$0^{2,7}$]undec-2-en-4-ones **8** and **9** were prepared by methylation of the morpholine enamine of **2**. After separation, base-catalyzed equilibration showed that the resulting mixture contained 80% of the 5β-methyl isomer **8**, and 20% of the 5α-methyl isomer.


6


7


8


9

The powerful effect of the presence of a methyl group at C(3) on the chemical shift of H–C(1) can be seen from *Table 1*; the close approach of C(1) and C(3) is also reflected in the production of a NOE on H–C(1) of **2** when H–C(3) is irradiated. The presence of a $(CH_3)\alpha$–C(5) group in **9** must result in some distorsion of the cyclohexenone ring towards a boat shape. Thus *Table 2* shows a lowering of the coupling constant $J(6\beta,7)$ (*i.e.* a narrowing of the dihedral angle) and a rise in the coupling constant $J(6\alpha,7)$.

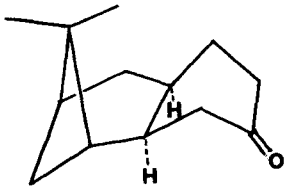
Catalytic reduction of a β-pinene such as **2** would normally be expected to lead to addition of hydrogen on the α-face of the molecule [14], but this would give a highly strained molecule, and we therefore examined the reaction. Hydrogenation over Pd/C led to the uptake of one mol-equiv. of hydrogen, with formation of a single product, to which we assign the all-*cis* configuration **10**. By a combination of double irradiation and europium shift techniques, the chemical shifts of most of the protons were established *(Table 3)*, and some confirmation was obtained by deuterium exchange experiments. Only 2–3 protons exchanged, indicating some

Table 3. *^{1}H-NMR. signals of tricyclo[7.1.1.$0^{2,7}$]undecanones* (the same conventions are used as in *Table 1*)

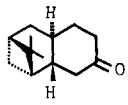
Substance	Proton on								
	C(1)	C(2)	C(3)α	C(3)β	C(4)α	C(4)β	C(5)α	C(5)β	C(6)α
10	1.93	?	(2.15)	2.72	–	–	(2.15)	2.43	2.45
11	1.63	1.92	2.22	2.21	–	–	2.30	2.52	?
19	1.82	2.31	1.90	1.65	2.21	2.47	–	–	(2.3)

Substance	Proton on								
	C(6)β	C(7)	C(8)α	C(8)β	C(9)	C(11)			
10	1.80	2.31	2.23	1.62	1.98	1.28	2.31	1.01	1.22
11	(1.57)	?	?	1.57	1.98	1.69	2.11	0.80	1.25
19	(2.3)	(2.3)	1.44	(2.3)	1.99	1.20	2.19	0.95	1.23

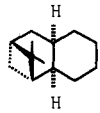
unusual situation for the fourth proton *a* to the carbonyl group. The configuration was confirmed by observing a NOE on H_β–C(3), H_β–C(6), H_β–C(8), H–C(1) and H–C(9) when the *syn*-methyl group was irradiated. This fact also means that the cyclohexanone ring must be boat-shaped. Reduction of 'Tricyclone' (**2**) with lithium in liquid ammonia also led principally to the *r*-1, *c*-2, *c*-7-ketone **10**, although in this case a trace of the *r*-1, *t*-2, *c*-7-ketone **11** was also isolated. *Wolff-Kishner* reduction of **10** led to the parent *r*-1, *c*-2, *c*-7-hydrocarbon **12**,



10

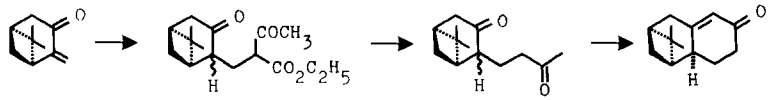


11

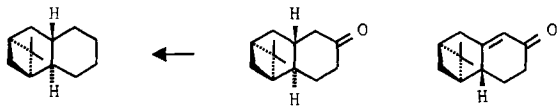


12

which was not identical with the *r*-1, *t*-2, *c*-7-hydrocarbon **13**, prepared from pinocarvone **14**[2]) as follows: *Michael* reaction of ethyl acetoacetate with pinocarvone **14** followed by hydrolysis and decarboxylation (without isolation) of the intermediate ketoester **15** yielded a mixture of isomers of the diketone **16**. The two isomers were not separated but cyclized directly to the isomer **17** of 'Tricyclone' (**2**).



14 **15** **16** **17**



13 **19** **18**

The product obtained is, of course, the base-catalyzed equilibrium mixture of isomers of **17**, but, unlike the 'Tricyclone' (**2**) case (where virtually only the *cis*-isomer was detectable [1]), *ca.* 10% of the *cis*-isomer **18** appeared as a shoulder in the gas chromatogram of **17**, and was also visible in the 360-MHz-NMR. spectrum of the product. The main isomer was nevertheless certainly *trans*, since irradiation of the *syn* methyl group produced a NOE on H–C(2) and H_β–C(8), the two most downfield protons, *i.e.* adjacent to the double bond. Catalytic hydrogenation of **17** gave the *r*-1, *t*-2, *c*-7-ketone **19**, *Wolff-Kishner* reduction of which yielded the hydrocarbon **13**, contaminated with a small amount of **12** (presumably the enantiomer) arising from the *cis* isomer **18**. It was more difficult to analyze the

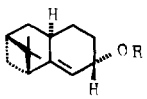
[2]) Although no particular attention was paid to the optical rotations of the compounds described, we in fact prepared **13** from (+)-*α*-pinene, so the compounds of this series have been drawn in the opposite absolute configuration from those derived from (−)-*β*-pinene *via* **1**. The *β*-face still means the same side of the molecule as the gem-dimethyl group.

Table 4. *^{13}C-NMR. signals of tricyclo[7.1.1.0^{2,7}]undecanes*

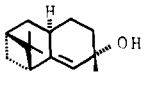
Substance	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
2	51.7	174.4	123.9	199.4	38.4	29.5	31.4	30.9
8	47.8	164.5	128.6	201.0	41.9	38.2	32.0	31.7
9	47.9	164.8	127.5	201.8	40.3	35.6	26.3	31.9
10	45.9	37.5	43.2	214.1	39.0	33.4	26.0	29.3
11	45.7	40.4	48.6	211.5	41.8	29.7	35.4	29.4
19	46.7	24.0	33.5	37.8	213.0	48.9	35.2	26.0
24	45.9	136.1	44.0	210.8	39.1	32.2	125.1	35.3
20	50.5	147.9	122.5	68.4	34.1	29.0	30.7	31.1

Substance	C(9)	C(10)	C(11)	*syn*-CH_3	*anti*-CH_3	other CH_3	
2	40.7	43.1	26.1	21.9	26.3		
8	40.8	43.3	25.8	21.4	26.6	10.4	15.8
9	40.9	43.6	25.9	21.4	26.7	10.3	16.2
10	41.3	39.2	28.0	22.7	28.0		
11	41.5	41.7	23.1	19.5	27.1		
19	40.9	33.7	24.9	20.0	26.0		
24	41.0	39.4	28.5	20.9	26.2		
20	41.2	42.6	26.0	21.6	26.4		

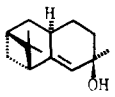
NMR. spectrum of the *r*-1, *t*-2, *c*-7-ketone because many protons appeared very close together. There is no doubt about its configuration, however, because of the mode of formation, and also the quite normal ^{13}C-NMR. spectra *(Table 4)*. Some improvement in the NMR. spectrum of **19** was achieved on adding pyridine, and irradiation of the *syn*-methyl group resulted in a NOE on H–C(2) and H_β–C(8) as expected. The chemical shifts of these protons were very close, and irradiation enabled H_a–C(8) to be placed well upfield in contrast to the chemical shifts of the C(8) protons in the *cis*-ketone **10**.



20 (R = H)
23 (R = $COCH_3$)



21

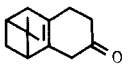


22

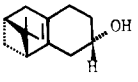
We obtained some evidence for the configuration of 'Tricyclone' (**2**) by a study of the spectra of the corresponding alcohols obtained by metal hydride reduction or *Grignard* addition to **2**. Lithium aluminum hydride reduction of **2** yielded a single alcohol, presumably **20**, formed by 'axial attack' [15] from the β face of the molecule, in agreement with experience using other octalones [16]. More useful was the reaction with methylmagnesium iodide, which yielded two alcohols (**21** and **22** *ca.* 5:1) which were separated by chromatography on silica gel. The less polar, minor isomer eluted first is ascribed the β-hydroxyl configuration **22** (a pseudo-axial hydroxyl group is normally less polar than a pseudo-equatorial one), and, in addition to the NMR. evidence discussed later, the configuration is supported by mass spectrometry. In the MS. of **22**, there is an appreciable molecular ion, together with an ion at *m/z* 191 (M^+-15), loss of water at *m/z* 188 representing 7.2% of the total ionization ($\sum_{40}$). The MS. of **21** shows almost no molecular or M^+-15 ion, and loss of water is 8.2% of $\sum_{40}$. The easier loss of water from **21** together with its less

stable molecular ion suggests that the hydroxyl group and the bridgehead proton at C(7) are on the same side of the ring [17].

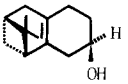
The NMR. results of the alcohols *(Table 1)* were obtained by decoupling experiments and addition of the shift reagent ($Eu(fod)_3$) at 360 MHz. It is notable that the bridgehead proton on C(7) is at lower field when it is on the same side of the molecule as the O-atom (compounds **20**, **21**, **23**) than when it is on the opposite side (**22**). The *syn*-methyl group shows the same effect, being at lower field in **22**. Although the shift reagent was useful in established first-order analyses of the proton spectra, the observed shifts were of little use in attributing configuration, the effects on distant parts of the molecule being fairly similar whichever side the O-atom was.



24



25



26

In the preparation of 'Tricyclone' (**2**) some 10,10-dimethyltricyclo[7.1.1.$0^{2,7}$]undec-2(7)-en-4-one (**24**) is produced [1]. Stereoselectivity during metal hydride reduction has been nearly lost in this compound, lithium aluminum hydride giving a mixture 60:40 of the two alcohols **25**, **26** that was very difficult to separate, but which was estimated by capillary GC. and by the ^{1}H-NMR. spectrum of the mixture. In this spectrum, the highest field methyl group was split into two signals at 0.78 ppm (major isomer) and 0.81 (minor isomer), the corresponding signals for the H(*syn*)–C(11) being at 1.18 (major) and 1.15 (minor). The compound with the higher field methyl signal would be expected to be the *trans* isomer **25**, an assignment that was supported when it was found that attempted catalytic hydrogenation of the allyl alcohol **20** led exclusively to a single isomer **25**, *i.e.* the double bond was rearranged to the sterically more favorable position rather than being reduced. Since this rearrangement does not involve C(4), the configuration of the single isomer observed in this case must be *trans* (**25**).

We are grateful to Mr. *R. Menghetti* and Mr. *P. Wetter* for assistance with the experimental work.

Experimental Part

General remarks. NMR. spectra were recorded in $CDCl_3$ on a *Hitachi-Perkin-Elmer* R20B (60 MHz), a *Bruker* HX-90 (90 MHz), or a *Bruker* WH-360 (360 MHz) instrument. Chemical shifts are given in ppm downfield from TMS (= 0 ppm), coupling constants *J* in Hz. Mass spectra were measured either on an *Atlas* CH-4 mass spectrometer using an inlet temperature of *ca.* 150°, or on a *MAT* 112 instrument coupled with a capillary gas chromatograph, both spectrometers using electrons of 70 eV. Results are quoted in *m/z* (% most important fragment), and generally the ten most important fragments are given. Column chromatography was carried out on *Merck* H (Type 60) silica gel using a *Jobin-Yvon* medium pressure gas chromatograph, and gas chromatography (GC.) on a *Carlo-Erba* type GT chromatograph with He as carrier gas.

Deuterium exchange of cis-*10,10-dimethyltricyclo[7.1.1.$0^{2,7}$]undec-2-en-4-one* (**2**) *and* cis-*10,10-dimethyltricyclo[7.1.1.$0^{2,7}$]undecan-4-one* (**10**) [4]. A small piece of sodium (0.1 g) was placed in dry dioxane (20 ml) and deuterium oxide was added dropwise until all the sodium had reacted. A total of

3 ml D_2O was used. Then 0.2 g of the ketone were added and the mixture heated at 70° for 3 h. After cooling, the products were isolated in pentane, and recovered after washing (D_2O), drying ($MgSO_4$) and concentrating. The deuterium content was determined mass-spectrometrically: from **2**; d_5 7%, d_4 54%, d_3 31%, d_2 7%, d_1 1.5%; from **10**; d_4 7%, d_3 36%, d_2 41%, d_1 12%, d_0 1%. A second exchange improved the figures for d_2 and d_3, but d_4 was still < 10%.

cis-*10,10-Dimethyltricyclo[7.1.1.0^{2,7}]undecane-4-one* (**10**). A solution of 55 g of 'Tricyclone' (**2**) in 550 ml of ethanol was hydrogenated over 5 g of 10% Pd/C. The theoretical amount of hydrogen was absorbed in 2 h, when the catalyst was filtered off, the solution was concentrated and the product distilled, b.p. 55–58°/0.001 Torr, $\alpha_D^{20} = -204°$ ($c = 11\%$, $CHCl_3$). – MS.: 91 (100), 133 (66), 41 (54), 69 and 79 (28), 55 (36), 67 and 134 (34), 95 (33), ...161 (8), 174 and 177 (7), 192 (7, M^+).

Reduction of **2** *with lithium in liquid ammonia.* To 250 ml of liquid ammonia were added 1.5 g of lithium in small pieces, then after stirring for 2 h, 10 g of 'Tricyclone' and 4.5 g of *t*-butyl alcohol were added dropwise. After 30 min, small portions of ammonium chloride were added (7.7 g in all), followed by 150 ml of ether, added while the ammonia was allowed to evaporate. The resulting ethereal solution was washed (water), dried and concentrated. The product was shown (GC.) to be *ca.* 96% **10**, but a trace of 10,10-dimethyl-2-*trans*-7-*cis*-tricyclo-[7.1.1.0^{2,7}]undecan-4-one (**11**) was isolated by GC. (retention time slightly shorter on a silicone oil column). – NMR. spectra are in the theoretical section. – MS.: 69 (100), 41 (96), 82 (82), 79 (80), 55 and 67 (77), 95 (74), 91 (65), 81 (62), 93 and 192 (57, M^+) ...177 (25).

1-(3-Oxopinan-10-yl)-acetones (**16**). To a solution of 520 g of ethyl acetoacetate and 30 g of sodium methoxide in 50 ml of absolute ethanol were added over 1 h 300 g of pinocarvone (**14**). The temperature rose from 39° to 62°. After 15 min more, there was no more pinocarvone, so the temperature was lowered (cooling) to 20° when 40 ml of glacial acetic were added followed by 100 ml ice-cold water and 200 ml of ethyl acetate. The organic layer was washed with brine (2 × 100 ml), and the solvents removed i.RV. The excess ethyl acetoacetate was removed at 75°/2 Torr, and the residue (536 g) distilled slowly with 1000 ml of dimethylformamide and 50 ml water. After 3 h, another 50 ml water were added, further amounts of 50 ml being added after 6 h and 9 h distillation (internal temp. 123–136°, distillation temp. 90–92°), after which time there was practically no ketoester left (GC.). After removal of the solvent, the residue was distilled, b.p. 107–135°/0.1 Torr. Yield 293 g (70%). For analysis, the material was purified by GC. *(Carbowax)*, which gave two incompletely separated peaks (*ca.* 7:3). – NMR. (60 MHz): 0.90, 1.34 and 2.15 (CH_3) with the minor isomer having the *anti*-CH_3 signal at 1.32. – MS.: 43 (100), 139 (35), 69 (26), 41 (25), 81 (17), 93 (12), 82 and 208 (11, M^+).

trans-*10,10-Dimethyltricyclo[7.1.1.0^{2,7}]undec-6-en-5-one* (**17**). A solution of 50 g of KOH and 300 g of the diketone **16** in 1000 ml of ethanol was heated for 30 min under reflux, then neutralized at 30° with glacial acetic acid. The alcohol was removed i.V., the residue was taken up in ethyl acetate, and the solution was washed with water (3 × 100 ml). The solvent was dried then evaporated, and the residue distilled, b.p. 97–105°/0.08 Torr, to yield 253 g (92%) of the title product, *ca.* 95% by GC. *(Carbowax)* containing *ca.* 5% of the *cis*-isomer. $\alpha_D^{20} = +8°$ (neat). – NMR.-spectra in theoretical part. – MS.: 91 (100), 190 (98, M^+), 119 (97), 147 (96), 133 (74), 41 (65), 105 and 148 (64), 134 (57).

2-trans-6-cis-*10,10-Dimethyltricyclo[7.1.1.0^{2,7}]undecan-5-one* (**19**). A solution of 19 g of the unsaturated ketone **17** in 200 ml of cyclohexane was hydrogenated over 0.5 g of 10% Pd/C. The theoretical amount of hydrogen was absorbed in 10 h. After filtration and concentration of the solution, the product was distilled, b.p. 78–80°/0.05 Torr. Yield 16.5 g (87%). Careful redistillation gave a product for which only one peak was visible on GC. *(Carbowax)*, $\alpha_D^{20} = -133°$ (neat). – NMR.-spectra are in the theoretical part. – MS.: 82 (100), 69 (76), 41 (73), 55, 67, and 134 (57), 91 (52), 95 (51), 79 and 131 (50) ...192 (19, M^+).

All-cis-*10,10-dimethyltricyclo[7.1.1.0^{2,7}]undecane* (**12**). A solution of 15 g of all-*cis*-10,10-dimethyltricyclo[7.1.1.0^{2,7}]-undecan-4-one (**10**) and 150 ml of hydrazine hydrate in 300 ml of diethyleneglycol and 300 ml of ethanol was heated under reflux for 15 min. After addition of 75 g of KOH, reflux was continued for 1 h, and the solution slowly concentrated over 3 h. The distillate was extracted with pentane, and the residue was diluted with water and extracted with pentane. The combined pentane extracts were washed with 10% hydrochloric acid then water, then concentrated and the residue distilled, b.p. 90–100°/10 Torr, yield 6.2 g. – ^{1}H-NMR. (360 MHz): 0.96 and 1.17 (each 3 H, CH_3); 1.29 (1 H, *d*, $J = 10$, H(*syn*)–C(11)); 2.18 (1 H, *m*, H(*anti*)–C(11)). – MS.: 67 (100), 135 (91), 41 (65), 82 (58), 81 (47), 79 (38), 55 (36), 69 (35), 93 (34), 95 (26)...163 (4), 178 (2, M^+).

2-trans-*7*-cis-*10,10-Dimethyltricyclo[7.1.1.0^{2,7}]undecane* (**13**) was prepared from 0.2 g of the ketone **19** by the procedure described in the foregoing experiment. The product was purified by GC. on silicone oil. – ^{1}H-NMR. (360 MHz): 0.89 and 1.19 (each 3 H, CH_3); 1.13 (1 H, *d*, $J = 10$, H(*syn*)–C(11)); 2.16 (1 H, *m*, H(*anti*)–C(11)); *ca.* 5% of the all-*cis* compound **12** was visible in the NMR. spectrum. – MS.: 135 (100), 67 (63), 81 and 82 (41), 41 (40), 79 and 93 (27), 69 and 95 (25), 55 and 121 (21)...163 (5), 178 (7, M^+).

cis-*3,10,10-Trimethyltricyclo[7.1.1.0^{2,7}]undec-2-en-4-one* (**6**). A solution of 30 g of norpinone (**1**), 52 ml of freshly distilled morpholine and 0.4 g of *p*-toluenesulfonic acid in 150 ml of dry toluene was refluxed for 18 h with separation of the water formed. The solution was concentrated, then at room temperature 23.5 g of pent-1-en-3-one was added. After stirring overnight, a further 4 ml of pent-1-en-3-one was added, and another 7 ml after 24 h more. Stirring at room temperature was continued until no more enamine was observed (GC.), this needing another 48 h. The mixture was heated under reflux for 4 h with 100 ml of methanol and 45 ml of concentrated HCl-solution. The methanol was removed i.V., and the residue taken up in ether. The ethereal solution was washed (water, $NaHCO_3$-solution, water), dried and concentrated, and the residue was distilled, to obtain 24 g (53%) of the title product, b.p. 88–92°/0.01 Torr. For analysis, it was purified by GC. (silicone oil). – The NMR. spectra are discussed in the theoretical part. – MS.: 69 (100), 41 (93), 136 and 204 (M^+) (80), 161 (77), 162 (50), 91 (48), 55 (47), 133 (41), 83 (39).

cis-*5β,10,10-Trimethyltricyclo[7.1.1.0^{2,7}]undec-2-en-4-one* (**7**). To a solution of diisopropylamine (30 ml, dried over *Linde* 4 Å) in tetrahydrofuran (200 ml) at –78° was added butyllithium (80 ml of a solution 11% in hexane) followed by 19 g of 'Tricyclone' (**2**) in 50 ml of tetrahydrofuran over 20 min. The mixture was allowed to come to 0° when methyl iodide (15 g) was added dropwise. The mixture was stirred for 2 h at 0°, then 16 h at 20° before being poured onto ice. The product was isolated in ether, washed (HCl-solution 10%, water), dried, and the ether concentrated to yield a residue (19 g) that was purified by chromatography on silica gel. There were first eluted *ca.* 3 g of a mixture of non-conjugated ketones (NMR., no vinyl proton) which was not further examined, followed by 14.2 g of material showing a single peak on GC. (silicone oil), but which 360-MHz-NMR. showed to contain in addition to the title product, *ca.* 5% of the 5*α*, 10,10-trimethyl isomer (see theoretical part). – MS. of pure 5*β*-methyl isomer: 41 (100), 69 (75), 162 (47), 91 (40), 121 (32), 119 (28), 204 (M^+) and 136 (22), 120 (18), 147 (15).

cis-*3,5β,10,10-Tetramethyltricyclo[7.1.1.0^{2,7}]undec-2-en-4-one* (**8**) *and* cis-*3,5α,10,10-tetramethyltricyclo[7.1.1.0^{2,7}]undec-2-en-4-one* (**9**). A mixture of 'Tricyclone' (**2**, 10 g), morpholine (8.7 g) and *p*-toluenesulfonic acid (0.2 g) in 150 ml of toluene was refluxed for 24 h, then concentrated and distilled, b.p. 95–100°/0.001 Torr. A solution of 30 g of the dienamine thus prepared and 30 g of methyl iodide in 300 ml of acetonitrile was heated under reflux and under nitrogen for 24 h. The mixture was washed (10% HCl-solution, water) and concentrated, and the residue distilled, b.p. 80–86°/0.001 Torr to yield 10.6 g of crude methylated products. This mixture was further purified by chromatography on silica gel. After a mixture of unconjugated ketones, crystalline **8** was eluted, m.p. 80–81°. – For the NMR. spectrum, see theoretical part. – MS.: 69 (100), 41 (80), 135 (60), 175 (49), 150 (45), 218 (40, M^+), 176 (38), 105 (34), 91 and 147 (30). Immediately after this, liquid **9** was eluted. These compounds were not readily separable on packed GC. columns, and the MS. were measured by capillary-GC./MS. coupling. The MS. of **9** was practically identical with that of **8**. For the NMR. spectrum, see theoretical part.

Base-catalyzed equilibration of either ketone **8** or **9** yielded a mixture containing 80% **8** and 20% **9** (by capillary GC.).

cis-*10,10-Dimethyltricyclo[7.1.1.0^{2,7}]undec-2-en-4α-ol* (**20**). A solution of 5 g of 'Tricyclone' (**2**) in 50 ml of dry ether was reduced with 0.5 g of lithium aluminum hydride at RT. After 1 h, water was added dropwise until there was no further precipitate formed, then the solid was removed by filtration and the residue after evaporation was distilled, b.p. 72–73°/0.01 Torr. The product decomposed on GC., but was apparently pure (TLC.). $[\alpha]_D^{20} = -41°$ ($CHCl_3$). – For NMR. spectra, see theoretical part. – MS.: 131 (100), 41 (75), 105 (68), 91 (62), 98 (57), 144 (52), 69 (47), 39 (41), 68 and 174 (37)...192 (10, M^+).

The *acetate* **23** was prepared by treatment of 1 g of the alcohol **20** with 1 g of acetic anhydride in 0.6 g of pyridine at RT. for 24 h. The mixture was poured onto ice and 10% sulfuric acid, and the product was isolated as usual in pentane. After removal of the pentane, the acetate was distilled (bulb, bath temp. 135–150°). – For NMR. spectra, see theoretical part. – MS.: 131 (100), 43 (71), 105 (52),

91 (50), 174 (39), 71 (36), 41 (26), 104 (22), 101 and 106 (20)...192 (6, M-42$^+$), 234 (trace, M^+). The acetate decomposed on GC.

10,10-Dimethyltricyclo[7.1.1.0^{2,7}]undec-2(7)-en-4-ols (**25** and **26**) were made by $LiAlH_4$ reduction in ether of the ketone **24** [1], in the manner described in the foregoing experiment. The product after distillation (bulb, bath temp. 95–110°) showed two peaks on capillary GC. (UCON 5100), ratio *ca.* 4:6 but a single peak on packed columns (silicone oil), from which it was collected for spectral analysis. – NMR. (90 MHz): major isomer, 0.78 and 1.27 (2*s*, 2 CH_3); 1.18 (*d*, J=8, H(*syn*)–C(11)); 3.97 (br., H–C(4)). Minor isomer, 0.81 and 1.27 (2*s*, 2 CH_3); 1.15 (*d*, J=8, H(*syn*)–C(11)); 3.97 (br., H–C(4)). – MS.: 131 (100), 91 (24), 130 (15), 41 (14), 132 (13), 105 (12), 159 (8)...174 (4.5), 192 (3.5, M^+).

When the alcohol **20** from the previous experiment was shaken with platinum (*Adams's* catalyst) in acetic acid for 24 h, practically no hydrogen was absorbed. Filtration and concentration yielded the 4α-ol, **25**, identical (GC., NMR.) with the substance described above.

cis-*4,10,10-Trimethyltricyclo[7.1.1.0^{2,7}]undec-2-en-4-ols* (**21** *and* **22**). A *Grignard* reagent was prepared from 0.7 g of magnesium and 4.4 g of methyl iodide in 30 ml of ether, then 5 g of 'Tricyclone' (**2**) was added dropwise with cooling to maintain the temperature at 15–20°. After 1 h at RT., the mixture was poured onto saturated ammonium chloride solution, and the products isolated as usual in ether. The crude material was chromatographed on silica gel in hexane/ether 9:1. After a small amount of hydrocarbons in the first fraction, 1.5 g of material mainly consisting of impure 4β-hydroxy isomer **22** was eluted, followed by 2.5 g of practically pure 4α isomer **23**. For analysis, it was necessary to rechromatograph these materials, from which there was obtained *ca.* 0.4 g of the 4β-isomer, m.p. 108–110°; NMR. spectra in theoretical part. – MS.: 145 (100), 119 (77), 91 and 188 (46), 41 (31), 105 (29), 117 (28), 69 (23), 118 (22), 120 (21)...191 (10), 206 (4, M^+). The pure 4α-isomer **23** had m.p. 75–76°; NMR. spectra in theoretical part. – MS.: 145 (100), 119 (84), 188 (51), 91 (36), 118 (34), 117 (29), 105 (27), 41 (19), 120 (17)...191 and 206 (M^+) (trace, < 1%); see also theoretical part.

REFERENCES

[1] *Y. Bessière, M. Barthélémy, A. F. Thomas, W. Pickenhagen & C. Starkemann*, Nouv. J. Chim. *2*, 365 (1978).

[2] *M. Barthélémy & Y. Bessière-Chrétien*, Bull. Soc. Chim. Fr. *1974*, 1703.

[3] *M. Barthélémy, A. Gianfermi & Y. Bessière*, Helv. *59*, 1894 (1976).

[4] *A. F. Thomas*, 'Deuterium Labeling in Organic Chemistry, Appleton-Century-Crofts' (now Plenum Press), New York 1971, p. 186.

[5] *F. Kaplan, C. O. Schulz, D. Weisleder & C. Klopfenstein*, J. Org. Chem. *33*, 1728 (1968).

[6] *R. B. Bates & V. P. Thalacker*, J. Org. Chem. *33*, 1730 (1968).

[7] *R. J. Abraham, F. H. Bottom, M. A. Cooper, J. R. Salmon & D. Whittaker*, Org. Magn. Reson. *1*, 51 (1969).

[8] *Y. Bessière-Chrétien & C. Grison*, Bull. Soc. Chim. Fr. *1971*, 1454.

[9] *P. Teisseire, A. Galfré, M. Plattier & B. Corbier*, Recherches *15*, 52 (1966).

[10] *A. J. Baretta, C. W. Jefford & B. Waegell*, Bull. Soc. Chim. Fr. *1970*, 3899, 3985.

[11] *J. Fournier*, J. Chem. Res. (S) *1977*, 320; (M) *1977*, 3440.

[12] *C. Nishino & H. Takayanagi*, Agric. Biol. Chem. *43*, 2323 (1979).

[13] *E. Brown, J. Touet & M. Ragault*, Bull. Soc. Chim. Fr. *1972*, 212.

[14] *M. Barthélémy, A. Gianfermi & Y. Bessière*, Bull. Soc. Chim. Fr. *1976*, 1821.

[15] *M. Chérest & H. Felkin*, Tetrahedron Lett. *1968*, 2205.

[16] *W. G. Dauben & J. W. Ashmore*, Tetrahedron Lett. *1978*, 4487, and literature cited therein.

[17] *C. E. Brion & L. D. Hall*, J. Am. Chem. Soc. *88*, 3661 (1966).