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3,7-DISUBSTITUTED BICYCLO[3.3.1]NONANES—III[1]

SYNTHESIS AND CONFORMATION OF BICYCLO[3.3.1]NONANE-3α,7α-DICARBOXYLIC ACID, ITS DIMETHYL ESTER AND SOME OTHER 3,7-DISUBSTITUTED BICYCLO[3.3.1]NONANES; ADAMANTANE AS AN INTEGRATED HOLDING SYSTEM

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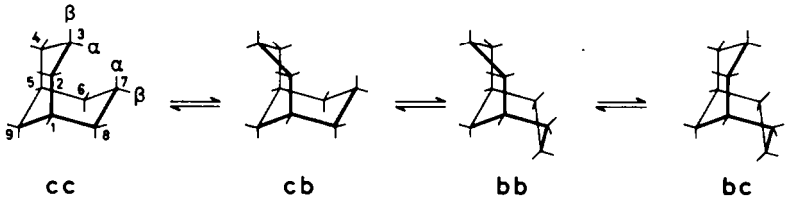
Abstract—The conformation of bicyclo[3.3.1]nonane-3α,7α-dicarboxylic acid and its dimethyl ester has been studied by comparing ^{1}H NMR and ^{13}C NMR spectra of these compounds with those of some model 3,7-disubstituted bicyclo[3.3.1]nonanes, fixed in a single conformation by the use of adamantane as an integrated holding group or by means of suitable substitution. It is shown that the dicarboxylic acid and its dimethyl ester exist predominantly as two rapidly interconverting (identical) chair-boat conformations with distinctly flattened rings; the population of the double-boat conformation appears to be very small.

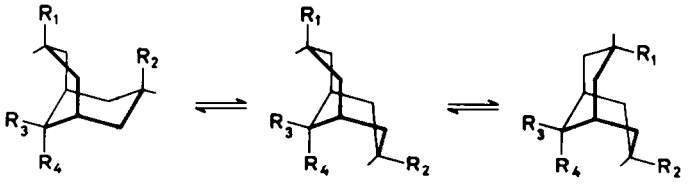
INTRODUCTION

Bicyclo[3.3.1]nonane as well as its 3β(7β)-substituted derivatives have been shown to exist in a somewhat flattened double-chair conformation (cc).[2] Severe transannular 3,7-interaction and 1,3-diaxial interactions destabilize the cc conformation in 3α(7α)-substituted bicyclo [3.3.1]nonanes. Consequently these compounds prefer a rigid chair-boat conformation (**cb**, **bc**).[2]



The enthalpy difference between the bicyclo[3.3.1]-nonane **cb** conformer and the double-boat conformer (**bb**) has been calculated to be 5·7 kcal/mole.[3] Therefore the conformational preference of 3α,7α-disubstituted bicyclo[3.3.1]nonanes will depend on the magnitude of the 1,3-diaxial interactions. The **bb** conformation will play a more important role when the bulk of the substituents increases; e.g. the diol **24** exists in the **bb** conformation,[4] whereas compound **13e** is in the **cb** conformation, with the ring containing the CO_2Me function in the boat.[1] In compounds **25** the population of the **cb** and **bb** conformers seems to depend on the size of the alkyl group.[5] The symmetrically substituted compounds bicyclo [3.3.1]nonane - 3α,7α - dicarboxylic acid (**4b**) and its dimethyl ester (**5b**) are very interesting from a conformational point of view. A previous ^{1}H NMR investigation[4] indicated that these compounds exist as an equilibrium of conformations, with an important contribution of the **cb** and **bc** conformations, possibly with flattening of the rings.

The present study deals with a comparison of ^{1}H NMR and ^{13}C NMR spectra of **4b** and **5b** with those of some other 3,7-disubstituted bicyclo[3.3.1]nonanes in order to verify these assumptions. As model compounds we used bicyclo[3.3.1]nonane derivatives constrained in a single conformation by building one of the rings into an adamantane skeleton, thus ensuring chair geometry of this ring, or by suitable substitution at the 3(7)-position.



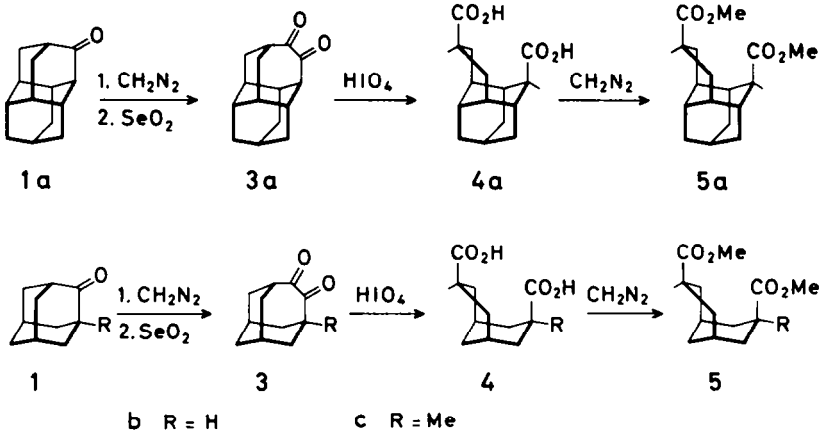
4b $R_1 = R_2 = CO_2H$; $R_3 = R_4 = H$ **13e** $R_1 = CO_2Me$; $R_2 = t\text{-}Bu$; $R_3, R_4 = O$
5b $R_1 = R_2 = CO_2Me$; $R_3 = R_4 = H$ **25** $R_1 = OH$; $R_2 = CH_2NR_xR_y$; $R_3 = R_4 = H$
24 $R_1 = R_2 = CMe_2OH$; $R_3 = R_4 = H$

Moreover a comparison was made between the 3,7-disubstituted bicyclo[3.3.1]nonanes and the previously studied 9-oxo derivatives.[1]

Synthesis

The dicarboxylic acids **4** were synthesized (Scheme 1) by means of a two step oxidative cleavage of the corresponding homoadamantanones,[4] which were obtained by ring enlargement of the adamantanones (**1**) with CH_2N_2.[7] Compounds **4** were converted into the corresponding dimethyl esters (**5**) with CH_2N_2.

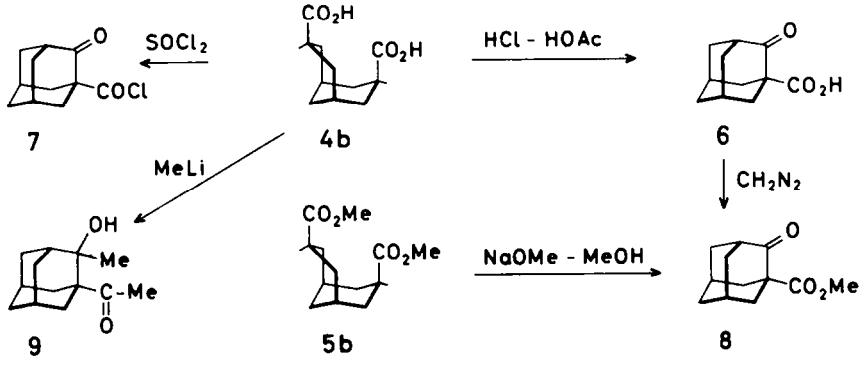
All traditional procedures to reduce the 9-oxo function in methyl 7 - alkyl - 9 - oxobicyclo[3.3.1]nonane - 3α - carboxylates (**13**)[1] failed, due to epimerisations and rearrangements. Therefore, after protection of the 9-oxo function as dimethyl acetal (**14**),[12] the 3α-CO_2Me function was reduced with LAH into the corresponding alcohol (**15**). Then the 9-oxo function was reduced by a Huang-Minlon procedure. Oxidation of the hydroxymethyl group with chromic acid in acetone, followed by esterification with CH_2N_2 afforded the methyl esters **19** (Scheme 4). It was observed that the oxidation of the



Scheme 1.

The configuration of compounds **4** and **5** allows facile ring closure in acidic as well as in alkaline medium. In Scheme 2 some examples are outlined. These procedures may serve as versatile synthetic routes towards 1,2-disubstituted adamantanes[8,9] and diamantanes.

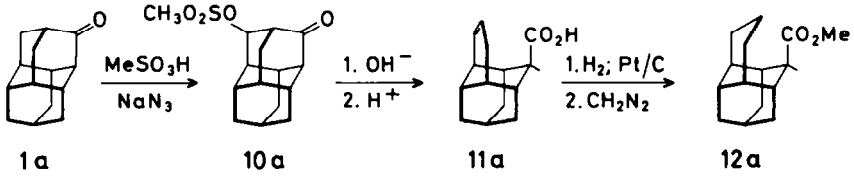
7β-alkyl derivatives (**16b, c**) produced almost quantitatively the acids **17b, c**, whereas for the 7α-alkyl derivatives (**16d,e**) the main product was the corresponding 3-oxo compound (**18**). The acid **17d** was obtained in low yield by oxidation of **16d** by O_2 with Pt as the catalyst.[13]



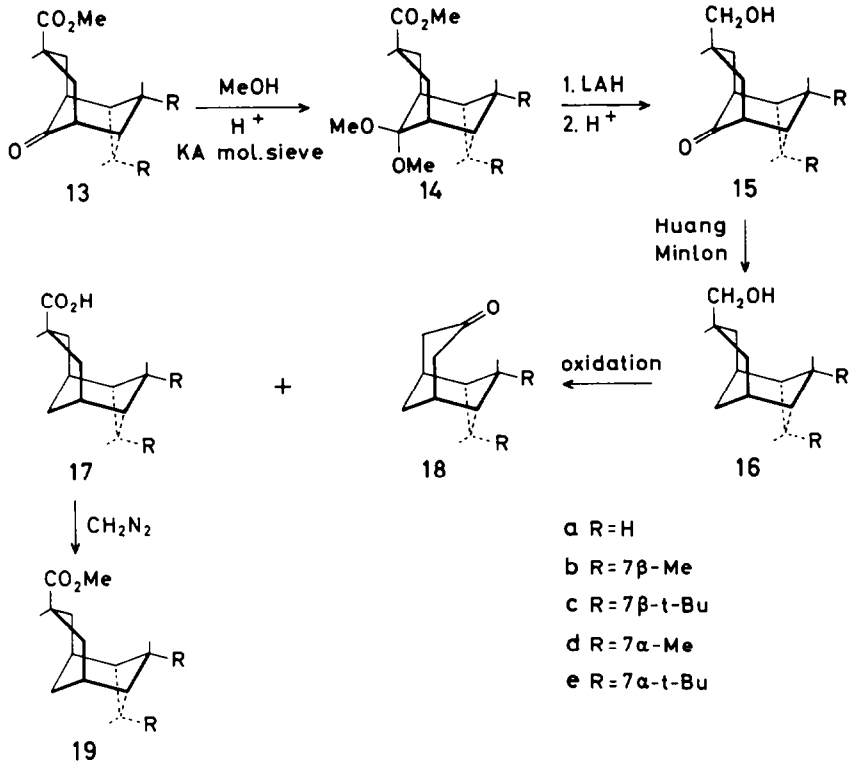
Scheme 2.

Treatment of diamantanone (**1a**) or adamantanone (**1b**) with NaN_3 in $MeSO_3H$ according to Sasaki *et al.*[10,11] yielded methanesulfonates (**10**), which, upon treatment with alkali, followed by hydrogenation and esterification gave the methyl esters **12**. In Scheme 3 this reaction sequence is outlined for compound **1a**.

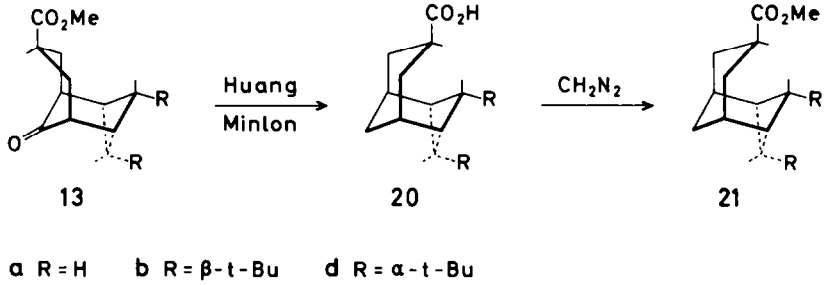
The methyl esters **21** were synthesized (Scheme 5) by means of Huang-Minlon reduction of the corresponding 9-oxo derivatives **13**, followed by esterification with CH_2N_2. The strong alkaline reaction medium caused epimerisation of the 3α-derivatives into the more stable 3β-compounds.



Scheme 3.



Scheme 4.



Scheme 5.

Reaction of compounds **19a**, **21a** and **5b** with MeMgCl gave the corresponding tertiary alcohols (**23**, **22** and **24**).

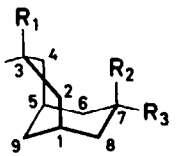
Conformational analysis

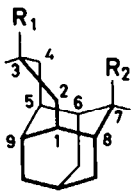
^1H NMR spectroscopy. The 100 MHz ^1H NMR spectrum of compound **5b** exhibits a sharp singlet for the protons of the two CO_2Me groups, a quintet for the 3α- and 7α-protons, a triplet for the 9-protons ($J = 3{\cdot}0$ Hz) and a complex signal for the other ring protons. The spectrum of the corresponding dicarboxylic acid **4b** is analogous to that of **5b**. At low temperatures (−90°) substantial line broadening occurs, showing that this compound exists as an equilibrium of conformations.

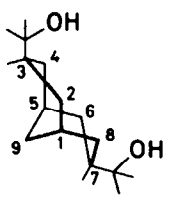
Spectra of **5b** were recorded with increasing amounts of Eu(dpm)$_3$ and Eu(fod)$_3$ until optimal separation between the various multiplets was achieved. From these spectra the coupling constants were derived by first-order analysis. The signals were assigned by the relative induced shifts, the splitting patterns, and by using double resonance techniques. These coupling constants were independent of the amount of shift reagent added, showing that the complexation had no observable influence on the conformation and geometry of **5b**. The coupling constants of **5b** and some related 3- and 3,7-substituted bicyclo[3.3.1]nonanes are listed in Table 1.

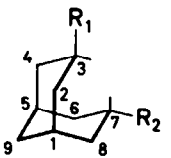
As should be expected,[1,14] the coupling constants of methyl bicyclo[3.3.1]nonane - 3α - carboxylate (**12b**) and its 7β-methyl (**19b**) and 7β - t - butyl (**19c**) derivative unambiguously prove that these compounds exist in the **cb** conformation with the ring containing the 3α-CO_2Me in the boat. Looking into more detail $J_{2\beta3\beta}$ differs from the value, that should be expected for an ideal rigid boat conformation (3·5–4 Hz). With the aid of the same procedure the corresponding coupling constant in methyl *trans* - 4 - t - butylcyclohexanecarboxylate was found to be 3·7 Hz. Apparently the boat ring in compounds **12b**, **19b** and **19c** is strongly flattened. Assuming that the HCH-angles retain the regular tetrahedral value, it can be calculated from $J_{2\beta3\beta}$ and $J_{2\alpha3\beta}$, by means of the semi-empirical version of the Pachler equations[15] as well as the Karplus equation (DAERM method[16]), that the dihedral angle between $H_{2\beta}$ and $H_{3\beta}$ is 47–50°. The

Table 1. Proton–proton coupling constants of 3- and 3,7-disubstituted bicyclo[3.3.1]nonanes (Hz)[b]









Compound No.	**5b**	**12b**	**19b**	**19c**	**5c**	**19d**	**18e**	**23**	**5a**	**12a**	**24**	**21a**	**21b**	**22**
R_1	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	Me	t-Bu	CMe_2OH	CO_2Me	H		CO_2Me	CO_2Me	CMe_2OH
R_2	CO_2Me	H	H	H	CO_2Me	CO_2Me	} = 0	H	CO_2Me	CO_2Me		H	t-Bu	H
R_3	H	H	Me	t-Bu	Me	H		H						
$J_{1,2\alpha}$	≤3	1–2	<4	≤6	2·3		<4	1·5	2·5	<4	2·0	2	<3	<3
$J_{1,2\beta}$	8·0	10·2	10·5	11·0	11·0		~11	11·0	11·0		10·0	4·0	4·5	4·0
$J_{2\alpha,2\beta}$	−14·0	−14·0	−14·0	−14·0	−14·0	~−12	−13·4	−14·0	−14·0	−12·9	−12·0	−14·0	−14·0	−13·3
$J_{2\alpha,3\alpha}$	—	—	—	—	—	—	—	—	—	6·0	—	5·3–6·0	5·7	5·5
$J_{2\alpha,3\beta}$	7·3	12·5	12·5	12·0	12·5	~12	13·1	13·3	12·0–13·0	<4	12·0	—	—	—
$J_{7\beta,3\alpha}$	—	—	—	—	—	—	—	—	—	12·0	—	12·6	12·4	12·7
$J_{2\beta,3\beta}$	6·8	6·0	6·0	6·3	6·0		4·7	5·6	6·4	~8	6·0	—	—	—
$J_{3\alpha,3\beta}$	—	—	—	—	—	—	—	—	—	−14·5	—	—	—	—
$J_{1,8\alpha}$	≤3				2·3	<4	<3		≤4		2·0			
$J_{1,8\beta}$	8·0		2·3		4·0	~5	4·7		—	—	10·0			
$J_{19,syn}$[a]	3·0				3·7		<4		≤4		2·5			2·5
$J_{19,anti}$[a]	3·0				2·5				≤4	—	2·5			2·5
$J_{6\alpha,6\beta}$	−14·0		−14·0	−12·6	−14·0	−13·5	−16·0		—	—	−12·0			~−13
$J_{6\alpha,7\alpha}$	—			3·7	—	—	—	4·2	—	—	—		—	5–6
$J_{6\alpha,7\beta}$	7·3		—	—	—	<3–4	—		≤3		12·0			
$J_{6\beta,7\alpha}$	—			12·3	—	—	—		—	—	—			
$J_{6\beta,7\beta}$	6·8		—	—	—	7	—	~12·5	—	—	6·0		—	
$J_{7\alpha,7\beta}$	—		—	—	—	—	—	~−12·5	—	—	—		—	
$J_{9,9}$	—				−13·0		−13·4		—	—	—			
$J_{9,syn2\alpha}$					1·5–2									

[a] syn and anti with respect to the 3-position.

[b] In order to make comparison simple, an unusual numbering is used.

flattening is somewhat more pronounced than in the corresponding 9-oxo derivatives.[1] There may be two reasons for flattening: the $H_{3\beta}$–H_9 repulsion and the eclipsing between H_1 and $H_{2\beta}$ and between H_5 and $H_{4\beta}$. When the CO_2Me group is replaced by a bulkier group as in compounds **18e** and **23** the flattening is diminished. Interaction between the bulky group and $H_{2\alpha}$ and $H_{4\alpha}$ possibly opposes flattening.

The dimethyl esters **5a** and **5c** are closely related to the problem under study. These compounds are constrained in a single **cb** conformation: in **5a** one of the rings is part of the rigid all-chair adamantane skeleton, whereas for **5c** the **bb** and the other **cb** conformation can be excluded because of strong destabilization by severe Me-9H repulsions. The coupling constants of the boat part of these systems are about the same as those for compounds **12b**, **19b** and **19c**. Apparently small changes in the geometry of the chair part of the molecule have no substantial influence on the flattening of the boat.

Compound **12a** is interesting: the coupling constants show that here, in spite of a large $H_{3\alpha}$-CO_2Me interaction, a flattened chair conformation is preferred.

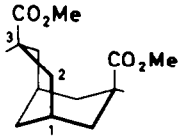
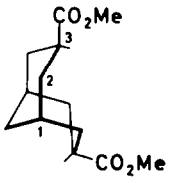
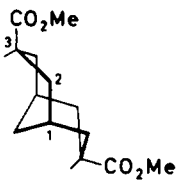
The coupling constants of the boat parts of compounds **12b**, **19b**, **19c**, **5a** and **5c** allow an estimation of the coupling constants of the boat part of the **cb** conformers of dimethyl bicyclo[3.3.1]nonane - 3α,7α - dicarboxylate (**5d**) (Table 2).

Diol **24** is the sole compound disposible, which doubtless exists in the **bb** conformation.[1] It might be expected that with a less bulky substituent (CO_2Me) at the 3α- and 7α-position, there is somewhat more flattening.†

In Table 2 estimated coupling constants of conformations of dimethyl bicyclo[3.3.1]nonane - 3α,7α - dicarboxylate (**5b**) are given. The estimated data for a rapid interconversion of the two (identical) **cb** conformations are in excellent agreement with the experimental values. A substantial contribution of the **bb** conformation can be excluded, since then $J_{2\alpha 3\beta}$ should be higher.

The lanthanide induced shift (LIS) parameters support this conclusion. In general the induced shifts are plotted versus the molar ratio shift reagent/substrate. We prefer, however, plotting the chemical shifts of the various protons versus the induced shift of one of the signals (e.g. the CO_2Me signal) with increasing amounts of shift reagent. Then for monofunctional as well as for bifunctional compounds excellent straight lines are generally obtained, which can provide-by means of extrapolation—the chemical shifts in the spectrum without shift reagent (δ_0). The slopes of these lines are dependent on the position of the proton in question *vis à vis* the coordinated Eu(III)-ion.[17] In Table 3 the slopes of these lines for several bicyclo[3.3.1]nonanes are given. For the dimethyl ester **5b** the influence of the shift reagent on the 2α-protons is relatively large, showing that the distance of

Table 2. The proton–proton coupling constants of dimethyl bicyclo[3.3.1]nonane-3α,7α-dicarboxylate

	Estimated values				Experimental values
	 A	 B	A ⇌ B		
$J_{12\alpha}$	<2·5	<4	<3	<2·5	≤3
$J_{12\beta}$	11·0	5	8·0	10–11	8·0
$J_{2\alpha 2\beta}$	−14·0	−14·0	−14·0	−12–−14	−14·0
$J_{2\alpha 3\beta}$	12·5	<3	6·2–7·2	11·5–12·5	7·3
$J_{2\beta 3\beta}$	6·0–6·4	7·0	6·5–6·7	6·0–6·4	6·8

An estimation of the coupling constants in the chair part of these conformations can be made from the appropriate coupling constants of compound **19d** (and in part **5c**). From the low value of $J_{1\beta 8\beta}$ and $J_{6\alpha 7\beta}$ and from the correspondence of the coupling constants with those of compound **18e** (which doubtless exists in the **cb** conformation), it may be concluded that **19d** is indeed predominantly in a **cb** conformation with the CO_2Me group in the chair. The value of $J_{6\beta 7\beta}$ suggests strong flattening of the chair, obviously due to the 1,3-diaxial interactions of the CO_2Me group with the other ring.

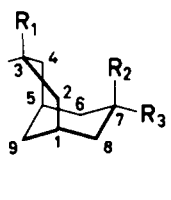
†Comparison of the coupling constants of **24**, **23**, **12b**, **19b**, **5c** and **5a** shows that the influence of this effect on the coupling constants is rather small. From a comparison of the rigid **cb** **23** with the flexible **bb** **24**, it may be concluded that also twisting (if present) should have rather small effects on the coupling constants. It should be noted that twisting affords a relief of $H_{3\alpha}$-H_9-strain, and a decrease of eclipsing, but on the other hand it introduces a severe interaction between $H_{2\alpha}$ and $H_{6\alpha}$ and between $H_{4\alpha}$ and $H_{8\alpha}$.

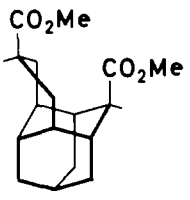
the Eu(III)-ion to these protons is rather small, especially compared to the 2β- and 3β-protons. This indicates that there has to be an important contribution of **cb** conformations (*cf.* compounds **19c**, **5c**, **5a** and **19d**).

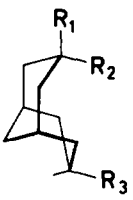
If the influence of the 7β-Me group is neglected, compound **5c** may be considered as a model for the **cb**'s in the conformational equilibrium of **5b**. The chemical shifts of two identical **cb** conformations in rapid interconversion can be estimated by averaging the chemical shifts of the corresponding protons in the chair and boat part of compound **5c** with increasing amounts of $Eu(dpm)_3$. These average chemical shifts were plotted versus the average chemical shifts of the 3- and 7-CO_2Me protons. Excellent straight lines were obtained. In Table 4 the slopes of these lines and the extrapolated (average) chemical shifts (δ_0) in the spectrum without $Eu(dpm)_3$ are given. The close agreement with the corresponding LIS-parameters of **5b** shows again that this compound exists predominantly in two rapidly interconverting **cb** conformations.

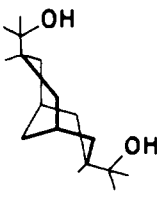
[13]*C NMR spectroscopy.* Recent results suggest that the

Table 3. Slopes of the lines of the chemical shifts of the various protons of 3(7)-substituted bicyclo[3.3.1]nonanes versus the induced shift of the signal of the 3-substituent with increasing amounts $Eu(fod)_3$



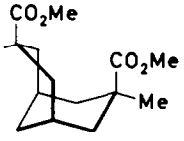




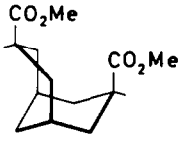


Compound No.	**5b**	**19c**	**5c**	**23**	**5a**	**19d**	**21d**	**20a**	**24**
R_1	CO_2Me	CO_2Me	CO_2Me	CMe_2OH		H	CO_2Me		
R_2	CO_2Me	H	CO_2Me	H		CO_2Me	H		
R_3	H	t-Bu	Me	H		Me	t-Bu		
H_1	0·51	0·22	0·40	0·17	0·31				0·39
$H_{2\alpha}$	1·34	0·80	2·04	0·68	1·98	0·94	0·79	1·00	0·90
$H_{2\beta}$	0·61	0·67	0·80	0·68	0·70	0·50	0·92	0·66	0·77
$H_{3\alpha}$	—	—	—	—	—	—	1·04	1·81	—
$H_{3\beta}$	1·16	1·09	1·31	0·99	1·00	1·19	—	—	1·10
$H_{4\alpha}$	1·34	0·18	0·71		0·71	0·81			0·90
$H_{6\beta}$	0·61		0·44		—				0·77
$H_{7\alpha}$	—	0·45	—	0·24	—	—	—	0·26	—
$H_{7\beta}$	1·16	—	—	0·20	1·00				1·10
H_{9syn}	0·38		0·35		0·43				0·36
H_{9anti}	0·38		0·38		—				0·36

Table 4. Comparison of LIS-parameters and extrapolated chemical shifts for compounds 5c and 5b



5c

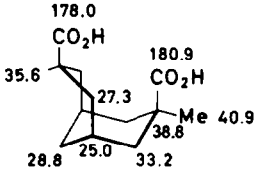


5b

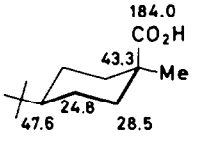
X	Y	$\Delta\delta_X + \Delta\delta_Y / \Delta\delta_{3\text{-}CO_2Me} + \Delta\delta_{7\text{-}CO_2Me}$	$\delta^\circ_X + \delta^\circ_Y/2$	$\Delta\delta_{X,Y} / \Delta\delta_{CO_2Me}$	$\delta^\circ_{X,Y}$
1	1	0.45	2.05	0.43	2.07
2 α	6 α	1.35	2.12	1.29	2.15
2 β	6 β	0.77	1.57	0.69	1.90
9syn	9anti	0.41	1.39	0.36	1.47

chemical shift of ^{13}C in a cyclohexane chair and boat conformation differs significantly.[18] A model compound for the **cb** conformation in the conformational equilibrium of **4b** is the dicarboxylic acid **4c** (Fig. 1). Supposing additivity, the influence of the methyl group on the ^{13}C chemical shifts can be computed by comparison of **26**[19] and **27**.[20]

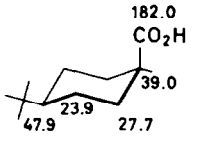
From these values and from the ^{13}C chemical shifts of **4c**, the ^{13}C chemical shifts of a **cb** conformation of **4b** were calculated. The averages of the corresponding chemical shifts for the chair- and boat-part represent calculated δ-values for a rapid interconversion of the two **cb** conformations. As shown in Table 5 excellent agreement exists with the experimental ^{13}C chemical shifts.



4c†



26



27

Fig. 1. ^{13}C chemical shifts (δ relative to TMS) of some model compounds ($CDCl_3$–DMSO-d_6 solution at 35°).

†The assignments of C_2 and C_6 might be reversed, but this has no influence on the calculation of the chemical shifts of **4b**.

Table 5. ^{13}C chemical shifts for compound **4b** (ppm relative to TMS)

Carbon atom	1	2	3	9
Calculated	24·1	29·8	35·1	29·0
Experimental	24·0	29·8	34·7	28·5

CONCLUSIONS

The ^1H NMR, LIS- and ^{13}C NMR-data provide strong evidence that bicyclo[3.3.1]nonane - 3α,7α - dicarboxylic acid and its dimethyl ester exist predominantly as two rapidly interconverting **cb** conformers. From a comparison of the vicinal HH-coupling constants it can be concluded that both the chair- and the boat-part of these **cb** conformers are distinctly flattened.

EXPERIMENTAL

The 60 MHz ^1H NMR spectra were recorded on a Varian T-60 or a Varian A-60 apparatus. The 100 MHz ^1H NMR spectra were obtained with a Varian XL-100-15 NMR spectrometer system, equipped with a V-4415 universal probe, in the CW-mode and the 25·2 MHz ^{13}C NMR spectra with the same apparatus in the FT-mode. The ^{13}C NMR peaks were assigned by off-resonance decoupling and by the chemical shifts. The spectra were recorded at 39°. Chemical shifts of both the ^1H- and ^{13}C-resonances are given in ppm (δ) relative to TMS.

The Lanthanide shift reagents Eu(dpm)$_3$ and Eu(fod)$_3$ were obtained from Merck.

The mass spectra were recorded by Messrs B. van de Graaf, P. J. W. Schuijl and H. M. A. Buurmans with a Varian-MAT SM-1 spectrometer at 70 eV using a direct insertion probe.

Elemental analysis were performed by Messrs M. van Leeuwen, M. A. Hoefnagel and H. M. A. Buurmans and were correct within 0·2% (absolute).

Ring enlargements. According to the procedure of Black and Gill,[7] **1a**,[21,22] **1b** and **1c**[23] were converted with CH_2N_2 and BF_3 as the catalyst into the corresponding homoadamantanones (**2**). For **2a**[24] and **2c** a mixture of the two structural isomers was obtained. The crude products, which had a GLC purity of >95%, were used for the next reaction step without further purification.

SeO_2-*Oxidations.* The crude product of the preceding reaction step (0·08 mole) was boiled with 9·85 g (0·09 mole SeO_2) in 45 ml dioxane and 1·9 ml H_2O for 6 hr. After filtration of the selenium comps, the solvents were evaporated off, yielding almost quantitatively **3a**, **3b**[6] and **3c**, respectively. These compounds were used without further purification.

HIO_4-*Oxidations.* The crude **3** was heated at 70° with 31 g (0·14 mole) $HIO_4 . 2H_2O$ in 260 ml dioxane–H_2O (3:1) for 45 hr. Then most of the solvent was evaporated *in vacuo*. The residue was dissolved in 100 ml EtOAc. The soln obtained was washed with a sat thiosulfate soln (4 × 100 ml) and then extracted with 2N KOH (4 × 80 ml). The KOH soln was washed with hexane (2 × 80 ml) and then acidified with 12N HCl. The dispersion obtained was extracted with EtOAc (5 × 80 ml). The EtOAc soln was washed with H_2O (2 × 80 ml) and dried over $MgSO_4$. After evaporation of the solvent chromatographically pure **4** was obtained. Further purification was achieved by recrystallisation and sublimation *in vacuo*. When the reaction was performed starting from pure **1b**, the yield of **4b** was 85%.

The dicarboxylic acids were converted into the corresponding dimethyl esters with CH_2N_2. *Decahydro* - 1,5,3 - [1,2,3] - *propanetriylnaphthalene* - 7α,9α - dicarboxylic acid (**4a**); m.p. 216–217° (from EtOAc–CH_2Cl_2). *Dimethyl decahydro* - 1,5,3 - [1,2,3] - *propanetriylnaphthalene* - 7α,9α - *dicarboxylate* (**5a**); ^1H NMR (60 MHz, CCl_4): δ 3·70 (3H, s), 3·57 (3H, s), 1·6–2·35 (18H). *Bicyclo*[3.3.1]*nonane* - 3α,7α - *dicarboxylic acid* (**4b**); m.p. 180·5–181° (from light petroleum–EtOAc); ^1H NMR (100 MHz, $CDCl_3$–DMSO-d_6): δ 12·53 (2H, s), 2·51 (2H, quintet: J = 7·2 Hz), 1·7–2·3 (10H), 1·43 (2H, t: J = 3·0 Hz). *Dimethyl bicyclo*[3.3.1]*nonane* - 3α,7α - *dicarboxylate* (**5b**); ^1H NMR (100 MHz, $CDCl_3$): δ 3·63 (6H, s), 2·48 (2H, quintet: J = 7·2 Hz), 1·7–2·3 (10H), 1·42 (2H, t: J = 3·0 Hz). 3β-*Methylbicyclo*[3.3.1]*nonane* - 3α,7α - *dicarboxylic acid* (**4c**); m.p. 216–218° (from light petroleum–EtOAc); ^1H NMR (60 MHz, CCl_4–DMSO-d_6): δ 11·28 (2H, s), 0·8–2·9 (14H), 1·07 (3H, s). *Methyl* 3β - *methylbicyclo*[3.3.1]) *nonane* - 3α,7α - *dicarboxylate* (**5c**); ^1H NMR (100 MHz, CCl_4): δ 3·68 (3H, s), 3·55 (3H, s), 1·12 (3H, s), 0·9–2·7 (13H).

2 - *Oxoadamantane* - 1 - *carboxylic acid* (**6**). In a sealed tube **4b** (508·8 mg; 2·40 mmole) was heated with 20 ml of a mixture of HOAc and 12N HCl (3:1) at 150° for 24 hr. The mixture was diluted with 30 ml H_2O and then extracted with EtOAc (5 × 20 ml). The EtOAc soln was washed with H_2O (3 × 20 ml) and dried over $MgSO_4$. After evaporation of the solvent 440·4 mg (2·23 mmole, 93%) chromatographically pure **6** was obtained. Further purification was achieved by recrystallisation from light petroleum (b.p. 40–60°) and sublimation (160°/10 mm); m.p. 166–167°; ^1H NMR (60 MHz, CCl_4–DMSO-d_6): δ 8·60 (1H, s), 1·7–2·8 (13H).

2 - *Oxoadamantane* - 1 - *carbonyl chloride* (**7**). Compound **4b** (587·5 mg, 2·77 mmole) was boiled with 15 ml $SOCl_2$ for 1 hr. Then the excess $SOCl_2$ was evaporated *in vacuo*. Dry benzene (15 ml) was added and removed again *in vacuo* to yield **7** (570·0 mg; 2·70 mmole, 97%). The pattern of the ^1H NMR signals was characteristic for 1-substituted 2-oxoadamantane derivs. The structure was confirmed by treatment of **7** with MeOH. After the usual work-up methyl 2 - oxoadamantane - 1 - carboxylate was obtained. This compound was identical with the authentic sample.

Methyl 2 - *oxoadamantane* - 1 - *carboxylate* (**8**). Acid **4b** (512·6 mg, 2·42 mmole) was esterified with CH_2N_2. The resulting methyl ester was boiled in a soln of 200 mg Na in 25 ml MeOH for 24 hr. The mixture was diluted with 25 ml H_2O. The dispersion obtained was extracted with pentane (4 × 15 ml). The pentane soln was washed with H_2O (3 × 10 ml) and dried over $MgSO_4$. After evaporation of the solvents almost pure **8** (492·9 mg; 2·37 mmole, 99%) was obtained. Further purification was achieved by recrystallisation from light petroleum; m.p. 86–86·5°; mass spectrum: important peaks at *m/e* 208, 180, 176 and 148; ^1H NMR (60 MHz, CCl_4): δ 3·68 (3H, s), 1·75–2·70 (13H).

The same ester was obtained after reaction of **6** with CH_2N_2 and after reaction of **7** with MeOH.

1 - *Acetyl* - 2 - *methyladamantan* - 2 - *ol* (**9**). Acid **4b** (1·01 g, 4·76 mmole) was dissolved in 20 ml THF. At 0° 40 ml of a 1·02M soln of MeLi in ether was added dropwise. The mixture was boiled for 3 hr. After cooling 50 ml H_2O was added. The layers were separated. The aqueous layer was extracted with EtOAc (4 × 30 ml). The combined organic layers were washed with 30 ml 2N KOH and with H_2O (2 × 30 ml). After drying over $MgSO_4$ and evaporation of the solvents 404·5 mg product was obtained. Recrystallisation from light petroleum and sublimation (95°/17 mm) gave pure **9**; m.p. 99–100°; mass spectrum: important peaks at *m/e* 208, 193, 190 and 165; ^1H NMR (60 MHz, CCl_4): δ 4·00 (1H, s), 2·12 (3H, s), 1·27 (3H, s), 1·1–2·5 (13H).

Work-up of the KOH-layer gave starting material (**4b**) besides **6**.

Reaction of diamantanone (**1a**) *and adamantanone* (**1b**) *with* NaN_3 *and* $MeSO_3H$.[10,11] To a suspension of the ketone in 25 ml $MeSO_3H$ 0·70 g (10·65 mmole) NaN_3 was added in the period of 1 hr. After 5 hr the mixture was poured on to 100 g ice. The suspension obtained was extracted with CH_2Cl_2 (5 × 50 ml). The CH_2Cl_2 soln was washed with H_2O (2 × 50 ml) and dried over $MgSO_4$. Evaporation of the solvent gave crude **10a**[11] (contaminated with the Beckmann rearrangement product) and **10b**[10] (which was used in the next reaction step without further purification). From the former mixture the aza products were removed by crystallisation from light petroleum (b.p. 80–110°). From the mother liquors the solvent were evaporated off. The residue was used in the next step without further purification.

Reaction of 4 - *methylsulfonoxydiamantan* - 2 - *one* (**10a**) *and* - *adamantan* - 2 - *one* (**10b**) *with alkali.*[10,11] The crude product of the preceding step was heated at 80° with 75 ml 2N KOH for 2 hr. The dispersion obtained was washed with $CHCl_3$ and acidified with 12N HCl and then extracted with $CHCl_3$ (4 × 30 ml). The $CHCl_3$ soln was washed with H_2O (2 × 30 ml) and dried over $MgSO_4$. Evaporation of the solvents gave almost pure **11b**[10] or the corresponding derivative **11a**.[11]

Hydrogenation of the unsaturated acids **11**. Crude **11** (0·50 g)

was hydrogenated in 20 ml EtOAc over 200 mg 10% Pd/C at 50° and 1 atm H_2. The catalyst was filtered off and the solvent was evaporated yielding almost pure decahydro - 1,5,3 - [1,2,3]propanetriylnaphthalene - 9α - carboxylic acid or bicyclo[3.3.1]nonane - 3α - carboxylic acid. Further purification was achieved by recrystallisation from light petroleum and sublimation. The methyl esters were obtained by reaction of the acids with CH_2N_2. *Decahydro - 1,5,3 - [1,2,3] - propanetriylnaphthalene - 9α - carboxylic acid*; m.p. 218–219°. *Methyl decahydro - 1,5,3 - [1,2,3] - propanetriylnaphthalene - 9α - carboxylate* (**12a**); ^{1}H NMR (60 MHz, CCl_4): δ 3·63 (3H, s), 2·50 (2H, broad s), 2·42 (2H, broad s), 0·9–2·1 (15H). *Bicyclo[3.3.1]nonane - 3α - carboxylic acid*; m.p. 127–127·5°; ^{1}H NMR (60 MHz, CCl_4): δ 12·12 (1H, s), 1·0–2·9 (15H). *Methyl bicyclo[3.3.1]nonane - 3α - carboxylate* (**12b**); ^{1}H NMR (100 MHz, CCl_4): δ 3·62 (3H, s), 2·49 (1H, t of t: J = 12·5 Hz and J = 6·0 Hz), 0·9–1 (4H), 0·5–0·9 (10H).

Methyl 7 - alkyl - 9,9 - dimethoxybicyclo[3.3.1]nonane - 3α - carboxylates (**14**). Compound 13[1] (0·04 mole) was stirred with 10 g MeOH and 2·50 g *p*-TsOH in 100 ml dry heptane at 10°. The stirrer was stopped and 15 g molecular sieve KA was added. After 1 min the stirrer was started again. After 30 min 2·50 g *p*-TsOH and 5·0 g KA-powder were added. After another 10 min the mixture was filtered and the sieve was washed with heptane. The heptane filtrate was washed with sat $NaHCO_3$ aq (2 × 80 ml) and H_2O (2 × 80 ml) and then dried over $MgSO_4$. Evaporation of the solvents gave the dimethyl acetals. According to ^{1}H NMR the 7β-alkyl derivs were pure, while the 7α-alkyl derivs were contaminated with starting compound (24%). Distillation or recrystallisation did not improve the purity. *Methyl 9,9 - dimethoxybicyclo[3.3.1] - nonane - 3α - carboxylate* (**14a**); b.p. 93–94°/0·5 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·60 (3H, s), 3·13 (3H, s), 3·07 (3H, s), 1·1–2·8 (13H). *Methyl 7β - methyl - 9,9 - dimethoxybicyclo[3.3.1]nonane - 3α - carboxylate* (**14b**); b.p. 120–122°/0·3 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·60 (3H, s), 3·14 (3H, s), 3·07 (3H, s), 1·0–2·1 (12H), 0·88 (3H, d: J = 7 Hz). *Methyl 7β - t - butyl - 9,9 - dimethoxybicyclo[3.3.1]nonane - 3α - carboxylate* (**14c**); m.p. 57·5–58° (from light petroleum); ^{1}H NMR (60 MHz, CCl_4): δ 3·62 (3H, s), 3·12 (3H, s), 3·07 (3H, s), 1·1–2·2 (12H), 0·80 (9H, s). *Methyl 7α - methyl - 9,9 - dimethoxybicyclo [3.3.1]nonane - 3α - carboxylate* (**14d**); b.p. 173–174°/21 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·65 (3H, s), 3·12 (3H, s), 3·07 (3H, s), 1·0–2·9 (12H), 0·82 (3H, d: J = 7 Hz). *Methyl 7α - t - butyl - 9,9 - dimethoxybicyclo[3.3.1]nonane - 3α - carboxylate* (**14e**); b.p. 113–114°/0·3 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·63 (3H, s), 3·12 (3H, s), 3·07 (3H, s), 1·0–2·9 (12H), 0·75 (9H, s).

7 - Alkyl - 9 - oxobicyclo[3.3.1]nonane - 3α - methanols (**15**). The reaction product of the preceding step was dissolved in 25 ml ether and added dropwise to a suspension of LAH (3·0 g; 0·08 mole) in 90 ml ether. The mixture was boiled for 3 hr. After cooling 15 ml EtOAc, 15 ml H_2O and 200 ml 4N H_2SO_4 were added dropwise subsequently. The aqueous layer was extracted with EtOAc (3 × 70 ml). The combined organic layers were washed with H_2O (2 × 70 ml) and then dried over $MgSO_4$. Evaporation of the solvents yielded **15** (90–95%). The 7α - alkyl derivs were contaminated with the corresponding 9-OH derivs. Purification was achieved by distillation (**15d**) or by fractionated crystallisation of the impurity from light petroleum–EtOAc and subsequent evaporation of the solvents from the mother liquors (**15e**). *9 - oxobicyclo[3.3.1]nonane - 3α - methanol* (**15a**); b.p. 90°/0·5 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·44 (2H, broad d), 0·9–2·8 (14H). *7β - Methyl 9 - oxobicyclo[3.3.1]nonane - 3α - methanol* (**15b**); b.p. 120–122°/0·3 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·80 (1H, broad s), 3·37 (2H, broad d), 0·9–2·8 (12H), 0·98 (3H, d: J = 6 Hz). *7β - t - Butyl - 9 - oxobicyclo[3.3.1]nonane - 3α - methanol* (**15c**); m.p. 91–91·5°; ^{1}H NMR (60 MHz, CCl_4–DMSO-d_6): δ 4·00 (1H, t: J = 6·5 Hz), 3·28 (2H, d of t: J = ~4·2 Hz and J = 6·5 Hz), 1·1–2·7 (12H), 0·92 (9H, s). *7α - Methyl - 9 - oxo - bicyclo[3.3.1]nonane - 3α - methanol* (**15d**); b.p. 132–134°/0·5 mm; ^{1}H NMR (60 MHz, CCl_4): δ 4·2 (1H), 3·34 (2H), 1·0–2·7 (12H), 0·95 (3H). *7α - t - Butyl - 9 - oxobicyclo[3.3.1]nonane - 3α - methanol* (**15e**); b.p. 155–160°/1 mm; ^{1}H NMR (60 MHz, DMSO-d_6): δ 4·73 (1H, s), 3·45 (2H, broad d), 1·1–2·7 (12H), 0·90 (9H, s).

7 - Alkylbicyclo[3.3.1]nonane - 3α - methanols (**16**). Compound **15** (0·027 mole) was boiled with 4 ml 100% hydrazine and 5·40 g KOH in 40 ml triethyleneglycol for 1·5 hr. Then the mixture was distilled until a bottom temp. of 210° was reached. Subsequently the mixture was boiled for another 4 hr. After cooling the mixture was diluted with 70 ml H_2O and combined with the distillate. The mixture obtained was extracted with ether (5 × 30 ml). The ether soln was washed with sat NaCl aq (3 × 30 ml) and dried over $MgSO_4$. Evaporation of the solvents gave the 7 - alkylbicyclo[3.3.1]nonane - 3α - methanols in about 85% yield. Further purification was achieved by distillation or by recrystallisation. IR spectra showed the absence of a CO-function. *Bicyclo[3.3.1]nonane - 3α - methanol* (**16a**); b.p. 88–90°/0·2 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·90 (1H, s), 3·33 (2H, d: J = 5·2 Hz), 0·8–2·2 (15H). *7β - Methylbicyclo[3.3.1]nonane - 3α - methanol* (**16b**); b.p. 127–128°/8 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·75 (1H, s), 3·32 (2H, d: J = 5·5 Hz), 0·5–2·5 (14H), 0·83 (3H, d: J = 6 Hz). *7β - t - Butylbicyclo[3.3.1]nonane - 3α - methanol* (**16c**); m.p. 65·5–66·5°; ^{1}H NMR (60 MHz, CCl_4): δ 3·47 (1H, s), 3·33 (2H, d: J = 6 Hz), 0·5–2·4 (14H), 0·83 (9H, s). *7α - Methylbicyclo [3.3.1]nonane - 3α - methanol* (**16d**); b.p. 142–143°/15 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·82 (1H, s), 3·40 (2H, d: J = 5 Hz), 0·5–2·4 (14H), 0·93 (3H, d: J = 6 Hz). *7α - t - Butylbicyclo [3.3.1]nonane - 3α - methanol* (**16e**); b.p. 183–185°/15 mm; ^{1}H NMR (60 MHz, CCl_4): δ 3·83 (1H, s), 3·36 (2H, d: J = 5 Hz), 0·6–2·3 (14H), 0·80 (9H, s).

7β - Alkylbicyclo[3.3.1]nonane - 3α - carboxylic acids (**17a, b, c**) *and methyl esters* (**19a, b, c**). At 10° 60 ml Jones reagent (26·7 g CrO_3 in 23 ml 100% H_2SO_4, diluted with H_2O to 100 ml) was added dropwise to a soln of 0·048 mole of **16** in 180 ml acetone. The mixture was then stirred at room temp. for 1 hr. After cooling until 0°, 240 ml MeOH was added. After 15 min stirring 450 ml H_2O was added. The dispersion obtained was extracted with $CHCl_3$ (5 × 100 ml). The $CHCl_3$ soln was washed with H_2O (3 × 100 ml) and dried over $MgSO_4$. After evaporation of the solvents the acids **17a–c** were obtained in about 95% yield. Further purification was achieved by recrystallisation from light petroleum. The methyl esters were synthesized by reaction of the acids with CH_2N_2. *Bicyclo[3.3.1]nonane - 3α - carboxylic acid* (**17a**);[14] m.p. 126·5–127°; ^{1}H NMR (60 MHz, CCl_4): δ 10·43 (1H, s), 0·9–2·7 (15H). *Methyl bicyclo[3.3.1]nonane - 3α - carboxylate* (**19a**); ^{1}H NMR (100 MHz, CCl_4): δ 3·62 (3H, s), 2·49 (1H), 1·0–2·2 (14H), *7β - Methylbicyclo[3.3.1]nonane - 3α - carboxylic acid* (**17b**); m.p. 107·5–108°; ^{1}H NMR (60 MHz, CCl_4): δ 11·73 (1H, s), 0·5–2·8 (14H), 0·85 (3H, d: J = 6 Hz). *Methyl 7β - methylbicyclo[3.3.1]nonane - 3α - carboxylate* (**19b**); ^{1}H NMR (60 MHz, CCl_4): δ 3·62 (3H, s), 0·7–2·8 (14H), 0·89 (3H, d: J = 6·5 Hz). *7β - t - Butylbicyclo[3.3.1]nonane - 3α - carboxylic acid* (**17c**); m.p. 150·5–151°; ^{1}H NMR (60 MHz, CCl_4): δ 14·63 (1H, s), 0·8–2·7 (14H), 0·83 (9H, s). *Methyl 7β - t - butylbicyclo[3.3.1]nonane - 3α - carboxylate* (**19c**); m.p. 36–37° (from light petroleum); ^{1}H NMR (100 MHz, CCl_4): δ 3·61 (3H, s), 2·44 (1H, t of t: J = 12·0 Hz and J = 6·3 Hz), 0·8–2·4 (13H), 0·84 (9H, s).

7α - Alkylbicyclo[3.3.1]nonane - 3α - carboxylic acids (**17d, e**) *and methyl esters* (**19d, e**). To a soln of **16** (3·54 mmole) in 25 ml heptane, was added 720 mg PtO_2. At 25° and 1 atm H_2 the catalyst was reduced. Then the H_2 was replaced by N_2, which was subsequently replaced by O_2. The temp. was raised until 80°. The reaction was followed by GLC. After 1 week no further conversion occurred. The catalyst was filtered off and washed with EtOAc. The filtrate was extracted with 2N KOH (3 × 15 ml). The KOH soln was washed with ether (2 × 15 ml), acidified with 12N HCl and then extracted with ether (4 × 15 ml). The ether soln was washed with H_2O (2 × 15 ml) and dried over $MgSO_4$. After evaporation of the solvent the acid **17d, e** was obtained in 15–25% yield. Compound **17d** was used without further purification. All efforts to purify compound **17e** were not successful. The esters (**19d, e**) were obtained after reaction of the acids with CH_2N_2. *7α - Methylbicyclo[3.3.1]nonane - 3α - carboxylic acid* (**17d**); ^{1}H NMR (60 MHz, CCl_4): δ 11·04 (1H, s), 0·5–3·0 (14H), 0·83 (3H, d: J = 6 Hz). *Methyl 7α - methylbicyclo[3.3.1]nonane - 3α - carboxylate* (**19d**); ^{1}H NMR (60 MHz, CCl_4): δ 3·65 (3H, s), 0·5–3·0 (14H), 0·77 (3H, d: J = 5·8 Hz).

7α - t - Butylbicyclo[3.3.1]nonan - 3 - one (**18e**). The neutral

organic layers of the oxidation of **17e** were combined, washed with H_2O (3 × 15 ml) and dried over $MgSO_4$. The solvents were evaporated off and the residue was crystallized from light petroleum at −80°. Further purification was achieved by sublimation at 55°/0·1 mm; mass spectrum: important peaks at *m/e* 138, 95, 80; ^1H NMR (60 MHz, CCl_4): δ 0·8–2·8 (13H), 0·78 (9H, s).

7 - *Alkylbicyclo*[3.3.1]*nonane* - 3β - *carboxylic acids* (**20**) *and methyl esters* (**21**). Ester **13** (0·027 mole) was boiled with 4 ml 100% hydrazine and 6·35 g KOH in 50 ml triethyleneglycol for 1·5 hr. Then the mixture was distilled until a bottom temp. of 200° was reached. Subsequently the mixture was boiled for another 4 hr. The mixture was diluted with 300 ml H_2O and acidified with 180 ml 6N HCl. The acid was filtered off, washed with H_2O, dried and recrystallized from light petroleum–EtOAc. The methyl esters were obtained by reaction of the acids with CH_2N_2. 7β - *t* - *Butylbicyclo*[3.3.1]*nonane* - 3β - *carboxylic acid* (**20b**); m.p. 136·5–137°; ^1H NMR (60 MHz, CCl_4): δ 12·02 (1H, s), 3·06 (1H), 1·15–2·25 (13H), 0·83 (9H, s). *Methyl* 7β - *t* - *butylbicyclo*[3.3.1]*nonane* - 3β - *carboxylate* (**21b**); ^1H NMR (60 MHz, CCl_4): δ 3·68 (3H, s), 3·12 (1H), 1·15–2·20 (13H), 0·83 (9H, s). 7α - *t* - *Butylbicyclo*[3.3.1]*nonane* - 3β - *carboxylic acid* (**20d**); m.p. 152–152·5°; ^1H NMR (60 MHz, CCl_4): δ 11·88 (1H, s), 2·63 (1H), 0·6–2·2 (13H), 0·87 (9H, s). *Methyl* 7α - *t* - *butylbicyclo*[3.3.1]*nonane* - 3β - *carboxylate* (**21d**); ^1H NMR (60 MHz, CCl_4): δ 3·60 (3*H*, *s*), 2·61 (1*H*), 0·7–2·2 (13*H*), 0·86 (9*H*, *s*).

3 - [2 - (2 - *Hydroxypropyl*)]*bicyclo*[3.3.1]*nonane* (**22**, **23**). These compounds were synthesized analogously to compound **24**. 3β - [2 - (2 - *Hydroxypropyl*)]*bicyclo*[3.3.1]*nonane* (**22**); m.p. 116–118°; ^1H NMR (60 MHz, acetone-d_6): δ 2·87 (1H, s), 1·2–2·5 (15H), 1·08 (6H, s). 3α - [2 - (2 - *Hydroxypropyl*)]*bicyclo*[3.3.1]*nonane* (**23**); m.p. 82–83°; ^1H NMR (100 MHz, CCl_4): δ 0·9–2·2 (16H), 1·13 (6H, s).

3α,7α - *Bis* - 2 - (2 - *hydroxypropyl*)*bicyclo*[3.3.1]*nonane* (**24**). Dicarboxylic acid **4b** (513·4 mg, 2·42 mmole) was esterified with CH_2N_2. The ester was dissolved in 25 ml ether and added at 0° dropwise to 25 ml of a 3·2 M soln of MeMgCl in THF. The mixture was stirred at 0° for 1 hr and then boiled for 1 hr. The mixture was poured on to 200 g ice. The dispersion obtained was saturated with NH_4Cl and then extracted with EtOAc (5 × 30 ml). The EtOAc soln was washed with a sat thiosulfate soln (2 × 30 ml), with H_2O (2 × 20 ml) and dried over $MgSO_4$. Evaporation of the solvent gave 571·5 mg (2·38 mmole, 98%) **24**. Further purification was achieved by recrystallisation from light petroleum; m.p. 106–107°; mass spectrum; important peaks at *m/e* 204, 189, 164, 149, 121 and 59; ^1H NMR (100 MHz, $CDCl_3$): δ 1·18 (12H, s), 0·8–2·4 (16H).

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