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ON THE CONFORMATION OF 8-SUBSTITUTED BICYCLO [3.2.1] OCT-6-EN-3-ONES

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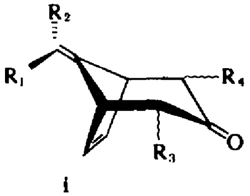
Abstract—A series of 8-substituted bicyclo [3.2.1] oct-6-en-3-ones (of type **i**) possessing various R_1 and R_2 groups were prepared and characterized. The conformations of the possible isomers of **1-4** were assigned according to the following three methods: (a) NMR spectrum, (b) time averaged precise metal ion location within the Eu $(dpm)_3$-carbonylic compound complex, (c) UV spectra. Comparison of the chair and boat conformers by UV spectra showed that interactions between the double bonds and the carbonyl occurred in both cases, although to different extents, the ϵ being dependent on R_1 and R_2. The fore-mentioned interaction exists even in both series of the C_6C_7 dihydro derivatives.

Being interested in the CD of substituted cyclohexanonic systems,[1] the investigation of 8-substituted bicyclo [3.2.1] oct-6-en-3-ones of type **i** was undertaken.

In the case of N-substituted tropinones the influence of the N-substituent of the Cotton effect of the CO has been well established.[1] It was thus interesting to see whether and to what extent such an influence could be observed in the absence of the polarizable C—N bond. To begin our research we chose the 8-substituted-bicyclo [3.2.1] oct-6-en-3-one (system **i**) for the following reasons.

Enhanced $n \rightarrow \pi^*$ transitions have been observed in the case of $\gamma\delta$-unsaturated ketones, showing that interactions even between the C=C and the C=O which are separated by a distance of three σ-bonds, occur.[2,3]

Labhart and Wagnière,[4] who have considered the coupling of olefin and CO groups in conjugated and unconjugated ketones, attributed this intensified $n \rightarrow \pi^*$ absorption to the mixing of the non-bonding p_n-orbital on the oxygen with the olefinic π_c-orbital which is of nearly the same energy. Of course, this interaction of donation and back-donation has a conformational dependence.[2a,3] In molecules of type **i** when $R_1 = R_2$, similar to the situation in hydrogenated bis-cyclopentadiene-benzoquinone derivatives investigated by Winstein[4] and some other polycyclic ketones like 7-norbornenone,[4] symmetry should cause the p_n–π_c overlap integral to be zero with each one of the double bonds, in the chair as well as in the boat conformation. Accordingly a charge transfer should be seen but enhancement of the $n \rightarrow \pi^*$ absorption is not to be expected. Nevertheless we thought it worthwhile to measure the UV spectra of molecules of type **i** when R_1 equals R_2 to find out if there is any difference between the various conformers, as well as to what extent the difference between various R_1 and R_2 groups will be seen in the $n \rightarrow \pi^*$ absorption. If such differences could be confirmed it should then be possible to undertake further investigation by CD of the optically active compounds, in which, contrary to the substituted tropinones[1] the R_1 and R_2 will be in a rigid position. An additional reason for choosing **i** was the assumption that due to the 4-methylenecyclohexanone embodied in the molecule the boat conformation would be almost as stable as the chair one[5] and according to the 6-membered ring substituents either the boat or chair form would be preferred. In a most recent publication by J. G. Vinter and H. M. R. Hoffmann[14] a chair-boat equilibria in one out of several, similar to **i**, bridged 16-oxatricyclo $[11.2.1^{2,12}]$ heptadec-14-en-17-one systems was indeed observed. Furthermore, at least in the boat conformation as in the molecules studied by Winstein,[4] overlap between the C_8—C_9 double bond and the CO is expected to exist and thus brings to light the difference between R_1 and R_2. Finally, but just as important was the synthesis of these compounds which have already been achieved principally by cycloaddition of 2,2-



i

1: $R_1 = R_2 = R_3 = R_4 = Me$
2: $R_1 = Me, R_2 = t\text{-}Bu; R_3 = R_4 = Me$
3: $R_1 = Me, R_2 = Ph; R_3 = R_4 = Me$
4: $R_1 = R_2 = Me; R_3 = R_4 = Ph$

dimethylcyclopropanone to 6,6-dimethylfulvene[6] or in lower yields by the reaction of 2-methoxyallyl cation with this fulvene.[7]

We found it most convenient to prepare the new compounds (**1–4**) by generating the 2-oxyallylic cation using α,α′-dibromo ketones with a zinc–copper couple[8] in the case of compounds **1–3** and with NaI[9] in the case of compound **4**. In all cases several isomeric cycloadducts (**a–c**) were obtained, their separation could be achieved by repetitive chromatography on acidic alumina or silicagel columns whereas on basic or neutral alumina rapid isomerisation occurs. This isomerisation could be monitored by GC, being performed under mild basic conditions, and was found to be complete after 24 hr yielding compounds **1a**, **1b**, **1c** in the ratio of 0·9:1:0·3 respectively; similar results were obtained for compounds **2–4**. Actually three methods were used in order to identify the various isomers: (a) Configurational assignment according to the NMR spectra. (b) Assignment according to the time averaged precise metal ion location within the Eu(dpm)$_3$-carbonylic compound complex, as calculated for the various conformational structures, from the values measured from the complex NMR spectra. (c) The use of UV spectra.

(a) The NMR spectra of compounds **1–4** in their various isomeric forms are given in Tables 1 and 2. From these data it can be seen that the identification of the 2α,4α-dimethyl *cis*-isomers caused no problems (Table 1) as the coupling constants ($J_{H_1H_{2\beta}}$ (or $J_{H_{4\beta}}H_5$) = 3 Hz) are adequate for a 60° dihedral angle between the corresponding protons.[9,10] In the 2β,4β-dimethyl *cis*-isomers the cyclohexanonic ring was expected to be in the boat conformation thereby releasing the 2β-Me, 4β-Me 1,3 diaxial interaction, and indeed the expected[10] *J*-values for this conformation were obtained ($J_{H_1H_{2\alpha}}$ ($J_{H_5H_{4\alpha}}$) = 0 ~ 1 Hz suits a dihedral angle of *ca* 100° between the respective protons, Table 2). In both *cis* isomer series the NMR spectrum showed no pronounced change with temperature (−110° – +30°), in contrast to the behavior observed in one of the *cis* isomers of the system investigated by Vinter and Hoffmann.[14] On the other hand the situation became more complicated with the *trans* isomers (Table 2) where the coupling constant between C-H-1 and C-H-2 on one side of the molecule was in accordance with the boat conformation while the corresponding protons on the other side of the molecule were in better agreement with the chair form. Comparison of **4c** ($J_{H_1H_{2\alpha}} = 3$, $J_{H_5H_{4\beta}} = 0$) (easily identified as the *trans*-isomer by the great difference between the two C-9-methyls, one being strongly diamagnetic shifted) with the *trans*-2α, 4β-diphenyl-bicyclo [3.2.1] oct-6-en-3-one[9] believed to be in the chair from ($J_{H_1H_{2\alpha}} = 2{\cdot}3$ and $J_{H_5H_{4\beta}} = 3{\cdot}0$ Hz) clearly indicated the different conformational situation. It is worthy to note that in **2** in spite of the large t-Bu group no deformation of the bicyclic-skeleton was noticed as can be seen from the *J*-values, and UV spectrum, *vide infra*.

(b) Lanthanide induced shifts (Δδ-values) can be calculated using the McConnell–Robertson expression for the pseudocontact shift[11] i.e. $\Delta\delta = k(3\cos^2\theta - 1)/r^3$ where r is the distance from the metal atom to the proton in question, θ is the angle made by this vector and the principal magnetic axis of the complex and k is a constant. Approximate, time-averaged, solution geometries for complexes formed by the interaction of Eu(dpm)$_3$ with ketones have already been estimated[12] and Eu-O distances ($d_{Eu\text{-}O}$) of 2·1 Å in unhindered ketones up to 3·9 Å in hindered ones (e.g. camphor) were found. The estimated ligand–metal complex geometries calculated in a similar way to the above previously mentioned one,[12] for compounds **1–3a–c** each in possible different conformers are presented in Table 3. As we were only interested in the relative $d_{Eu\text{-}O}$ values found in the different conformers, approximate coordinates were measured using Dreiding models, in this way, checking known compounds from the literature[12] showed that the error does not exceed 10–15%. In the case of 2α,4α-dimethyl *cis*-isomers (**1–3a**) the distinction between the chair ($d_{Eu\text{-}O} = 1{\cdot}8 \div 1{\cdot}9 \pm 0{\cdot}3$), boat ($d_{Eu\text{-}O} = 1{\cdot}1 \div 1{\cdot}4 \pm 0{\cdot}3$), and flattened form, in which c_1–c_5 are almost in the same plane, ($d_{Eu\text{-}O} = 1{\cdot}35 \pm 0{\cdot}3$) was clear, which was also the case of the other *cis*-isomers (**1–3b**) in which the difference between the chair ($d_{Eu\text{-}O} = 4{\cdot}70 \pm 0{\cdot}7$) and boat ($d_{Eu\text{-}O} = 1{\cdot}35 \pm 0{\cdot}3$) was tremendous. In the flattened conformation of **1–3b** the Eu-O distance ($d_{Eu\text{-}O} = 1{\cdot}6 \pm 0{\cdot}3$) increased somewhat. Thus the real conformation of the ring may be somewhat flattened (?). Of course using a more sophisticated computer program, estimation of the conformation should be more accurate. The results obtained for the *trans* isomers in the various conformers, show that none of the $d_{Eu\text{-}O}$ values were adequate, and most probably a mixture of conformers exists. Noteworthy is the fact that compounds **4a,c** do not undergo any complexation with Eu(dpm)$_3$, which can be explained by the reported steric environment effect on the complexation.[12]

(c) The last and most important method used for the conformer-differentiation, as far as further CD study was concerned, was the UV spectra. All the compounds display the expected n → π* and the charge-transfer π → π* absorptions with meaningful differences among them (Table 4). The high wave length absorption band appearing at 285–290 nm (ε = 25–36) in the case of the chair isomers (**1–3a**), clearly differs in the case of the boat forms (**1–3b**) which give rise to an 70–80% enhanced, red shifted absorption, as compared to **1-3a**, at 305–308 nm (ε = 46–62) together with a very characteristic fine structure (in contrast to **1–3a**). This low-intensity long wave length band was readily assignable as an n → π* transition on the basis of its low intensity and the shift of the maximum to

Table 1

Comp.	H1	H5	H2	H4	H6	H7	R1 (9 Me)	R2	R3	R4
1a	3·26 m		2·35 d(J = 3 Hz) of q(J = 7 Hz)		6·12 m		1·7 s	1·7 s	1·0 d (J = 7 Hz)	
2a	3·26 m	3·64 m	2·4 d(J = 3 Hz) of q(J = 7 Hz)	2·47	6·1 m		1·71 s	1·2 s	1·0 d (J = 7 Hz)	0·98 d
2a*	3·05 m	3·5 m	2·24 d(J = 3 Hz) of q(J = 6·8 Hz)	2·45	5·9 m		1·5 s	1·02 s	1·05 d J = 7	1·05 d
3a	3·12 m	3·44 m	2·54 d(J = 3 Hz) of q(J = 7·5 Hz)	2·65	6·18 m		2·05 s	7·2 m	0·94 d J = 7·5	1·12 d
4a	3·66 m		3·8 d(J = 3 Hz)		6·38 m		1·82 s	1·82 s	7·26 m	
5	2·82 m		2·5 d(J = 3 Hz) of q(J = 6·5 Hz)		1·52 m		1·76 s	1·76 s	1·0 d (J = 6·5 Hz)	
6†	2·25		2·5 m		1·45 m		1·0 d(J = 7 Hz)	1·0 d(J = 7 Hz)	0·95 d(J = 7 Hz)	
8	3·1 m	2·8 m	2·42 d(J = 3 Hz) of q(J = 7·5 Hz)	2·50	1·5 m		1·78 s	1·2 s	0·95 d	
9	3·28 m		3·85 d(J = 3 Hz)		1·9 m		1·85 s	1·85	7·2 m	
10	2·65 m		3·8 m		1·9 m		0·95 d(J = 7 Hz)	0·95 d(J = 7 Hz)	7·2 m	
11	2·45 m		2·0 m		1·9 m		0·95 d(J = 7 Hz)	0·95 d(J = 7 Hz)	1–2 m	

*Taken in C_6H_6.
†Most probably a mixture of the two 8-epimers.

Table 2

Comp.	H1	H5	H2	H4	H6	H7	R1 (9 Me)	R2	R3	R4
1b	3·12 m		2·35 br, q (J = 7·6 Hz)		6·08 m		1·75 s	1·75 s	1·08 d (J = 7·6 Hz)	
2b	3·65 m	3·20 m	2·30 d(J = 1 Hz) of q(J = 7·6 Hz)	2·38	6·05 m		1·7 s	1·2 s	1·10 d (J = 7·6 Hz)	1·17 d
3b	3·26 m	3·06 m	2·20 br, q(J = 7·6 Hz)	2·35	6·1 m		2·08 s	7·2 m	0·82 d (J = 7·5 Hz)	1·25 d
2c	3·65 m	3·20 m	2·40 d(J = 2·5 Hz) of q(J = 7 Hz)	2·60 d((J = 3·5 Hz) of q(J = 7 Hz)	6·1 m		1·7 s	1·2 s	0·96 d (J = 7 Hz)	1·12 d
3c	3·2 m	2·85 m	2·5[a] d(J = 1 Hz) of q(J = 7·5 Hz)	d(J = 3 Hz) of q(7·5 Hz)	6·1[b]		1·9 s	7·1 m	0·75 d (J = 7 Hz)	1·10 d
4c	3·56 m		3·85 d (J = 3 Hz)	3·95 (br, s)	6·45	6·28[b]	1·74 s	1·02 s	7·2 m	
7	2·8 m		2·45 (J = 7 Hz)		1·7 m		1·9 s	1·9 s	1·15 d (J = 7 Hz)	

[a] Seen only after complexation with Eu(dpm)$_3$.

[b] 8-line pattern, (ABCD) system.

Table 3

Comp.	Δδ	Δδ	Δδ	Δδ	Δδ	Δδ	Chair		Boat		Flattened conformer	
	H1, H5	H2, H4	H6, H7	R1	R2	2, 4 Me	d_{Eu-O}[a]	φ	d_{Eu-O}[a]	φ	d_{Eu-O}[a]	φ
1a	1·20	2·90	1·10	0·50	0·50	2·15	1·8	180°	1·3	180°	1·35	130°
2a	0·85	1·85	0·80	0·30	0·25	1·50	1·9	195°	1·1	180°	—	
3a	0·90	2·10	0·85	0·35	0·20	1·65	1·8	180°	1·4	180°	—	
1b	1·10	3·45	0·85	0·60	0·60	1·75	4·7	115°	1·3	180°	1·5	170°
2b	1·30	4·45	1·10	0·65	0·50	2·20	4·7	110°	1·3	180°	1·6	170°
3b	0·82	2·75	0·75	0·40	0·25	1·45	4·7	110°	1·3	180°	1·7	170°
2c	0·55	1·40 1·90	0·55	0·25	0·25	0·70 0·90	3·1	160°	1·1	180°	—	
3c	1·10	3·00 3·50	1·00	0·50	0·40	1·40 2·15	1·1	180°	1·7	180°	1·2	130°

All Δδ values are reported in PPM ($CDCl_3$), for $Eu(dpm)_3$/Substrate (R) ratio of 0·75; straight lines (Δδ *vs* R) were observed for all mentioned protons in the range of R ≃ 0·1–1.

[a] d_{Eu-O} = Eu ..... O═C distance (Å), and φ is the proper angle between these atoms.

Table 4

Comp.	λ max(ε) (n → π*)	λ max(ε) (π → π*)
1a	285 (25)	220' (2540)
1b	288 (35), 297 (44), *308 (46)* 317 (35), 326 (16)	220' (3200)
1b[a]	285 (43), *295 (45)*, 305 (43)	225' (1560)
2a	288' (36)	220' (5650)
2a[a]	278' (52)	230 (2300)
2b	325 (26), 316 (48), *305 (62)* 297 (61), 280 (59)	220' (3900)
2c	325 (22), 315 (44), *305 (55)* 295 (55), 286 (48)	220' (5650)
3a	290' (36)	238 (9850), 200 (22400)
3b	330 (18), 318 (38), *307 (50)* 298 (49)	235 (8250)
3c	315' (27), 305' (38), 295' (50) *290' (57)*	235 (6000)
4a	290' (43)	265 (740), 255 (1210), 250' (1650)
4c	298 (88)	266 (655), 260 (1100),254 (1490)
5	285 (28)	225 (1332)
6	285 (20)	
7	330 (13), 318 (28), *307 (39)* 298 (32), 292 (25)	210' (4240)
8	283 (33)	225 (2340)
8[a]	280 (31)	230 (1930)
9	290 (46)	265 (127), 255 (870), 250 (1680)
10	285 (38)	265 (380), 255 (510), 250 (510)
11	290 (17)	
12		end abs.

Cary 14 recording spectrophotometer. Spectra taken in isooctane. i–inflection.

[a] Taken in MeOH.

shorter λ with increasing solvent polarity. As expected the increase of ε within the same series (**1–3a** and **1–3b**) is proportional to the difference between R_1 and R_2. Hydrogenation of the C_6—C_7 double bond in **1a** and **4a** did not change the ε while in **1b** it was slightly diminished (Table 4, compounds **5**, **9** and **7** respectively); further reduction of the C_8—C_9 bond which was possible only in the chair conformers e.g. **1a** and **4a** to give **6** and **10** respectively lowered the ε somewhat more. In the case of **4a** hydrogenation in the presence of PtO_2 at 80 PSi reduced the two double bonds as well as the two phenyl groups (to give **11**) thereby reducing the ε to a value of 17, similar to that of **6**.

Quantitative information from the charge-transfer absorption at 220–240 nm (disappearing in the corresponding alcohols and shifting to longer wave length with increasing solvent polarity as expected[3]—in the case of **8** where the maximum is clear) was difficult to accept, as in most of the cases it appears ill defined as a shoulder. Nevertheless it was interesting to find that it still exists in the dihydro derivative of the chairs (**5** and **8**), proving further overlap between the C_8═C_9 and C═O bonds even in this conformer. Turning to the *trans* isomers (**2c** and **3c**) the same n → π* fine structure which was notable in the boat isomers (**1–3b**) again could be seen, and in the case of **2c** (where there is no interference of the phenyl as in **3c**) the ε, between the values found in case of **2a** (36) and **2b** (62), was 55 indicating a mixture of chair and boat conformations but not excluding, on the basis of the UV spectrum alone, a deformed boat if such a conformer can also give rise to this fine structure(?). The absorption of compound **4c** (298, ε = 88) in comparison to *trans* - 2α, 4β - diphenyl-bicyclo [3.2.1] oct - 6 - en - 3 - one[9] (298, ε = 120) can be interpreted in the same way.

On the basis of the similar population of the *cis*-chair and boat conformers after isomerisation, invariable NMR spectrum of the *trans* compound **4c** between $-110^\circ \div +30^\circ$ and the other evidence presented above it seems to us that the *trans* isomers appear in an equilibrium between chair and boat. We hope that the forthcoming investigation mentioned above will give more information.

EXPERIMENTAL

M.ps were taken on a Thomas and Hoover m.p. apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Infracord Model 337 spectrophotometer. NMR spectra were taken on a Varian HA-100 and Jeol JMN-C-60 HL spectrometers using 5–10% solns in $CDCl_3$ with TMS as an internal standard. Mass spectra were taken with a Hitachi Perkin-Elmer RMU 6 instrument. Purification by column chromatography was done on grade II acidic Al_2O_3 (Merck) eluted with light petroleum–benzene mixtures.

Gas chromatography was performed on a Packard Gas Chromatographed with all glass 1/4″/6 ft column with 3% OV-17 on GCQ 80–100 mesh. 120°–220°. The retention time was in the order **c** > **b** > **a**.

6,6-Dimethylfulvene, 6-phenyl-6-methylfulvene and 6-t-butyl-6-methylfulvene were prepared according to known procedures.[13]

(1) *Cycloaddition procedures*

(1) Debromination of α, α' - dibromo - 3 - pentanone with Zn–Cu couple *in situ*, as described,[8] and reaction with the proper substituted fulvenes.

(2) Reactions of di-(α-bromobenzyl) ketones with NaI and the suitable fulvenes, according to Cookson.[9]

Cis-2α, 4α-*Dimethyl-8-isopropylidene bicyclo* [3.2.1] *oct-6-en-3-one* (**1a**) *and* cis-2β,4β-*dimethyl-8-isopropylidenebicyclo* [3.2.1] *oct-6-en-3-one* (**1b**). Method 1 (60% yield) chromatography of the mixture gave the two isomers (eluted with light petroleum) **1a** and **1b** in ratio of ~5:1.

Compound **1a**, b.p. 100°/6 mm, ν_{max}^{neat} 1700, 1450, 1370, 1110, 920, 780, 750 cm^{-1}. (Found: C, 81·94; H, 9·33; $C_{13}H_{18}O$ requires: C, 82·06; H, 9·53%). Mass spectrum *m/e* 190 (72%, M^+), 134 (80%, M—$COCHCH_3$), 133 (33%), 119 (100%, 134-CH_3), 91 (47%).

Compound **1b** m.p. 60° (sub. 70°/5 mm), $\nu_{max}^{CHCl_3}$ 1700, 1450, 1360, 1140, 920 cm^{-1}. (Found: C, 81·80; H, 9·50; $C_{13}H_{18}O$ requires: C, 82·06, H, 9·35%). Mass spectrum undistinguishable from **1a**. Compound **1c** could not be isolated in a pure state.

cis - 2α, 4α - *Dimethyl* - 8 - (*methyl* - *t* - *butylmethylene*) *bicyclo* [3.2.1] *oct* - 6 - *en* - 3 - *one* (**2a**), cis - 2β, 4β - *dimethyl* - 8 - (*methyl* - *t* - *butylmethylene*) *bicyclo* [3.2.1] *oct* - 6 - *en* - 3 - *one* (**2b**) *and* trans - 2α, 4β - *dimethyl* - 8 - (*methyl* - *t* - *butylmethylene*) *bicyclo* [3.2.1] *oct* - 6 - *en* - 3 - *one* (**2c**). Method 1 (66% yield) elution of the mixture with light petroleum–benzene (8:2) gave the three compounds (**2a**, **2b**, and **2c**) in ratio of *ca* 20:1:1. Compound **2a**, b.p. 110°/1 mm, ν_{max}^{neat} 1700, 1460, 1380, 910, 795, 750 cm^{-1}. (Found: C, 82·60; H, 10·25; $C_{16}H_{24}O$ requires: C, 82·70; H, 10·41%). Mass spectrum *m/e* 232 (45%, M^+), 217 (44%, M—CH_3), 175 (100%, M—COC_2H_5) and 161 (96%). Compound **2b** b.p. 110°/1 mm, ν_{max}^{neat} 1700; 1460; 1380; 1170; 1140; 960; 920 cm^{-1}. Mass spectrum undistinguishable from **2a**. Compound **2c** b.p. 120°/1 mm, ν_{max}^{neat} 2950; 1700; 1500; 1460; 1380; 1330; 960; 920 cm^{-1}. Mass spectrum undistinguishable from **2a** and **2b**.

cis - 2α, 4α - *Dimethyl* - 8 - (α - *phenethylidene*) *bicyclo* [3.2.1] *oct* - 6 - *en* - 3 - *one* (**3a**) cis - 2β, 4β - *dimethyl* - 8 - (α - *phenethylidene*) *bicyclo* [3.2.1] *oct* - 6 - *en* - 3 - *one* (**3b**) *and* trans - 2α, 4β - *dimethyl* - 8 - (α - *phenethylidene*) *bicyclo* [3.2.1] *oct* - 6 - *en* - 3 - *one* (**3c**). Method 1 (60% yield), elution of the mixture with light petroleum:benzene (1:1) gave the three compounds (**3a**, **3b**, **3c**) in ratio of *ca* 5:1:traces. Compound **3a**, b.p. 100°/1 mm (m.p. 58°), ν_{max}^{neat} 1700, 1600, 1490, 1430, 1370, 1340, 1110, 1020, 920, 760, 700 cm^{-1}. (Found: C, 85·56; H, 7·81; $C_{18}H_{20}O$ requires: C, 85·67; H, 7·98%). Mass spectrum *m/e* 252 (45%, M^+), 196 (77%, M—COC_2H_4), 181 (100%, M—(COC_2H_4 + CH_3)); 165 (68%), 91 (30%). Compound **3b** an oil (decomposing on distillation) ν_{max}^{neat} 1700, 1600, 1490, 1430, 1370, 1110, 1020, 920, 760, 700 cm^{-1}.

Mass spectrum: undistinguishable from **3a**. Compound **3c** an oil (decomposing on distillation) ν_{max}^{neat} 1700, 1600, 1490, 1430, 1380, 1020, 920, 760. Mass spectrum undistinguishable from **3b** and **3c**.

cis - 2α, 4α - *Diphenyl* - 8 - *isopropylidene bicyclo* [3.2.1] *oct* - 6 - *en* - 3 - *one* (**4a**) *and* trans - 2α, 4β - *diphenyl* - 8 - *isopropylidene bicyclo* [3.2.1] *oct* - 6 - *en* - 3 - *one* (**4c**). Method 2 (~90% yield). Upon crystallization from acetone: light petroleum compound **4a** was obtained in a pure state, m.p. 148°. ν_{max}^{KBr} 1700, 1600, 1500, 1450, 1380, 1080, 850, 760, 630 cm^{-1}. (Found: C, 87·70; H, 6·84; $C_{23}H_{22}O$ requires: C, 87·86; H, 7·05%). Mass spectrum *m/e* 314 (50%, M^+), 195 (78%), 181 (100%), 91 (38%). Compound **4c** m.p. 109° (EtOH), ν_{max}^{KBr} 1700, 1600, 1500, 1450, 1030, 930, 780, 730 cm^{-1}. Mass spectrum undistinguishable from **4a**.

cis - 2α, 4α - *Dimethyl* - 8 - *isopropylidenebicyclo* [3.2.1] *octan* - 3 - *one* (**5**). Compound **1a** (200 mg) in EtOAc (20 ml) was hydrogenated over 10% Pd on $CaCO_3$ at room temp and atmo press for 48 h. The reaction was discontinued and the product, which was obtained following filtration and evaporation of the solvent, crystallised from light petroleum m.p. 52° (sub. 60°/0·5 mm) $\nu_{max}^{CHCl_3}$ 1700, 1430, 1360, 1120, 970 cm^{-1}. Mass spectrum *m/e* 192 (22%, M^+), 107 (100%), 106 (52%) and 91 (27%).

cis - 2α, 4α - *Dimethyl* - 8 - *isopropylbicyclo* [3.2.1] *octan* - 3 - *one* (**6**). Compound **1a** (200 mg) in EtOAc (20 ml) was hydrogenated over PtO_2 at r.t., 80 PSi for 48 h. Following the usual work up the tetrahydro derivative of **1a** was obtained, b.p. 75°/0·5 mm; $\nu_{max}^{CHCl_3}$ 1700, 1470, 1450, 1370, 1130, 1080, 980 cm^{-1}. Mass spectrum *m/e* 194 (60%), 137 (43%), 123 (50%), 95 (100%), 81 (54%) and 69 (54%).

cis - 2β, 4β - *Dimethyl* - 8 - *isopropylidenebicyclo* [3.2.1] *octan* - 3 - *one* (**7**). Compound **1b** (120 mg) was hydrogenated as described for **5**, the product was sublimated at 90°/1 mm, m.p. 25°; ν_{max}^{KBr} 1700, 1470, 1400, 1130, 1080 cm^{-1}. Mass spectrum undistinguishable from **5**.

cis - 2α, 4α - *Dimethyl* - 8 - (*methyl* - *t* - *butylmethylene*) *bicyclo* [3.2.1] *octan* - 3 - *one* (**8**). Compound **2a** (100 mg) was hydrogenated as described for **5** to give compound **8**; b.p. 105°/1 mm; ν_{max}^{neat} 1700, 1480, 1380, 1200, 1130, 1080, 975 cm^{-1}. (Found: M^+ 234; $C_{16}H_{26}O$ requires: 234).

cis - 2α, 4α - *Diphenyl* - 8 - *isopropylidene* [3.2.1] *octan* - 3 - *one* (**9**). Compound **4a** was hydrogenated as described for **5** to give the dihydro derivative **9**; m.p. 158° (MeOH), ν_{max}^{KBr} 1700, 1600, 1490, 1450, 1070, 1030, 750, 700 cm^{-1}. Mass spectrum *m/e* 316 (17%, M^+), 209 (97%), 131 (51%), 107 (100%), 93 (97%), 91 (63%) and 65 (97%).

cis - 2α, 4α - *Diphenyl* - 8 - *isopropylbicyclo* [3.2.1] *octan* - 3 - *one* (**10**). Compound **4a** was hydrogenated with 10% Pd on C under the same conditions as described for **6**, to give **10**, m.p. 192° (CH_3CN), ν_{max}^{KBr} 1700, 1600, 1500, 1450, 1190, 1070, 700 cm^{-1}. Mass spectrum *m/e* 318 (40%, M$^+$), 247 (22%), 117 (97%), 115 (40%) and 91 (100%).

cis - 2α, 4α - *Dicyclohexyl - 8 - isopropylbicyclo* [3.2.1] *octan - 3 - one* (**11**). Compound **4a** gave after hydrogenation under the same conditions as described for **6**, the dicyclohexyltetrahydro derivative **11**, m.p. 110° (acetone), ν_{max}^{KBr} 1700, 1470, 1450, 1130, 960, 885, 850 cm^{-1}. Mass spectrum *m/e* 330 (38%, M$^+$), 248 (100%, M—C_6H_{10}), 123 (38%), 109 (36%), 81 (53%), 67 (62%) and 55 (86%).

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