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Reduction of 7-Methylenebicyclo[3.3.1]nonan-3-one and Related Compounds: Structural Investigation of the Products

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Hydrogenation of 7-methylenebicyclo[3.3.1]nonan-3-one (**1**) over platinum oxide in acetic acid yielded 7α-methylbicyclo[3.3.1]nonan-3α-ol (**2**) as the sole product. Hydrogenation of (**1**) in ethyl acetate afforded 7α-methylbicyclo[3.3.1]nonan-3-one (**3**) as a reduced product and 7-methylbicyclo[3.3.1]non-6-en-3-one (**4**) as an isomerized product. Hydrogenation of **1** over palladium on carbon gave no reduced product but **4** in 100% conversion. Hydrogenation of 7-methylenebicyclo[3.3.1]nonan-3α-ol (**7**) and -3β-ol (**8**) over platinum oxide in acetic acid gave **2** and 7α-methylbicyclo[3.3.1]nonan-3β-ol (**5**), respectively. From studies based on NMR spectroscopy with use of a shift-reagent, it is concluded that the major conformer of **2** and **5** is of chair-boat form. By the equilibration experiment between **2** and **5** using aluminum isopropoxide in isopropyl alcohol at 110°C, the ΔG° value was found to be -2.2 kcal/mol.

In the bicyclo[3.3.1]nonane system, the preferred conformation is believed to possess a double chair form so long as the substitutents at C-3 and/or C-7 have β-configuration. Crystallographic investigation[1] has indicated that the preferred conformation of the bicyclo[3.3.1]nonane skeleton is of a double chair form in spite of the considerable interactions between the α-hydrogen atoms at C-3 and C-7. If this system takes predominantly such a preferred conformation, two interesting phenomena can be expected, a transannular reaction involving C-3 and C-7 and a steric effect toward the reagents. Examples of these phenomena have been given by many workers.[2] We have also reported on some novel transannular reactions.[3]

However, when a bulky substituent at C-3 has α-configuration, the substituted cyclohexane ring has been reported to exist in a boat conformation.[4-10] It has been reported that the symmetrically 3α,7α-disubstituted bicyclo[3.3.1]nonanes exist as an equilibrium mixture or in a double boat conformation owing to the bulkiness of the substituent.[11] The report prompted us to publish our study on the conformation of the compound unsymmetrically disubstituted at C-3 and C-7 both in α-configuration.

Catalytic hydrogenation of 7-methylenebicyclo[3.3.1]-nonan-3-one[12] (**1**) in acetic acid over platinum oxide gave exclusively 7α-methylbicyclo[3.3.1]nonan-3α-ol (**2**). However, hydrogenation in ethyl acetate gave 7α-methylbicyclo[3.3.1]nonan-3-one (**3**) and an isomerized product, 7-methylbicyclo[3.3.1]non-6-en-3-one (**4**). All the reductions gave stereospecifically α-substituted products. The geometry of the reduction product (**2**), in which both the hydroxyl and methyl groups have α-configuration, and that of the epimeric alcohol (**5**) were studied by NMR spectroscopy, analy-

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[1] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, **1965**, 1844; W. A. C. Brown, G. Eglington, J. Martin, W. Parker, and G. A. Sim., *Proc. Chem. Soc.*, **1964** 57; I. Laszlo, *Rec. Trav. Chim. Pays-Bas*, **84**, 251 (1965).

[2] For pertinent references see G. D. Buchanan, "Topics in Carbocyclic Chemistry," Vol 1, Ed. by D. Lloyd, Ed., Logos Press, London (1963), p. 236; R. C. Bingham and P. v. R. Schleyer, "Topics in Current Chemistry 18, Chemistry of Adamantane," Springer-Verlag, Berlin (1971); A. C, Cope, M. M. Martin, and M. A. Mc-Kervey, *Quart. Rev.*, (London), **20**, 119 (1966).

[3] a) T. Mori, K. Kimoto, M. Kawanisi, and H. Nozaki, *Tetrahedron Lett.*, **1969**, 3653, b) T. Mori, K. H. Yang, K. Kimoto, and H. Nozaki, *ibid.*, **1970**, 2419, c) M. Kawanisi and H. Kato, *ibid.*, **1970**, 721, d) K. Kimoto and M. Kawanisi, *Chem. Ind.* (London), **1971**, 1174.

[4] W. D. K. Macrosson, J. Martin, and W. Parker, *Tetrahedron Lett.*, **1965** 2589.

[5] a) C.-Y. Chen and R. J. W. Le Fèvre, *J. Chem. Soc. B*, **1966**, 539; b) C.-Y. Chen and R. J. W. Le Fèvre, *Tetrahedron Lett.*, **1965**, 737.

[6] E. N. Marvel and R. S. Knutson, *J. Org. Chem.*, **35**, 388 (1970).

[7] M. Fisch, S. Smallcombe, J. C. Gramain, M. A. McKervey, and J. E. Anderson, *ibid.*, **35**, 1886 (1970).

[8] M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, **1968**, 298.

[9] R. A. Appleton, D. H. G. C. Egan, J. M. Evans, S. H. Graham, and J. R. Dixon, *J. Chem. Soc. C*, **1968**, 1110.

[10] J. M. McEuen, R. P. Nelson, and R. G. Lawton, *J. Org. Chem.*, **35**, 690 (1970).

[11] D. A. Peters, J. D. Remijnse, A. van der Wiele, and R. van Bekkum, *Tetrahedron Lett.*, **1971**, 3065.

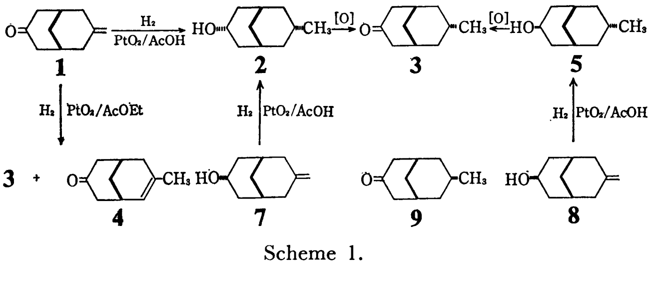
[12] A. R. Gagneux and R. Meier, *ibid.*, **1969**, 1365.

sis of the patterns of the carbinyl protons, and with a shift-reagent developed for expansion of the chemical shift to analyze the signals.[13] The preferred conformations of **2** and **5** were concluded to be of boat-chair form. Equilibration between **2** and **5** with aluminum isopropoxide in isopropyl alcohol at 110°C gave a mixture consisting of 94.6% of **5**. The $\Delta G°$ value was calculated to be −2.18 kcal/mol. This could be considered as the gross energy difference between the two 1,3-diaxial hydroxyl-methylene interactions of the distorted cyclohexanol ring in **2** and the two 1,3-diaxial methylene-hydrogen interactions of the chair form in **5** providing that the methylcyclohexane ring takes a boat form.

Results and Discussion

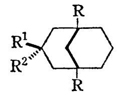
We have reported two new transannular reactions of **1**; photoreduction[3b] leading to 7-methyl-3-noradamantanol (**6**) and diimide reduction[3d] giving the same compound in high yield. Our observations suggest that **1** might exist predominantly in a double chair form. In such a case, catalytic hydrogenation may be expected to occur exclusively from the less hindered β-face of the substrate (**1**). Actually, when hydrogenation of **1** over platinum oxide was conducted in acetic acid, 7α-methylbicyclo[3.3.1]nonan-3α-ol (**2**) was obtained quantitatively and stereospecifically. The compound was also obtained as a sole product by the hydrogenation of 7-methylene-bicyclo[3.3.1]nonan-3α-ol (**7**)[8] under the same conditions, whereas the same hydrogenation of 7-methylenebicyclo[3.3.1]nonan-3β-ol (**8**)[8] afforded 7α-methylbicyclo[3.3.1]nonan-3β-ol (**5**). Configuration-α of the methyl group in **2** and **5** was established by the oxidation of either **2** and **5** to give the same compound, 7α-methylbicyclo[3.3.1]nonan-3-one (**3**), the structure of which was confirmed by the fact that the compound (**3**) differs from the known 7β-methylbicyclo[3.3.1]nonan-3-one (**9**)[14] in all respects. The configurational assignments of the hydroxyl groups were not only obvious from the reaction schemes, but were also confirmed by the observation that lithium aluminum hydride reduction of **3** gave a mixture of **2** and **5** in the ratio 4 : 1, since the reagent preferably attacks from the sterically less hindered β-face.[15]

Hydrogenation of **1** over platinum oxide in ethyl acetate gave 7α-methyl ketone (**3**) as the reduced product together with **4** resulting from the migration of the double bond. When this reaction was allowed to proceed to completion, **4** was converted slowly but exclusively into **3**. When the amount of the catalyst was reduced (0.01 mol ratio), **3** and **4** were obtained in the ratio 3 : 2. The structure of **4** was assigned on the basis of IR, NMR, and elemental analysis. The reaction was followed by glc, which shows that at 50% hydrogenation, **4** was already formed together with **3**, and when the reaction was allowed to proceed further the amount of **3** increased at the expense of **4**. Pure sample of **4** afforded **3** when allowed to react for an extended period under the same conditions. This shows unamibiguously that hydrogenation and isomerization compete in the reaction of **1** under neutral conditions. When **1** was refluxed in ethanol under an atmosphere of nitrogen for 24 hrs, an isomeric mixture (**1** : **4**=2 : 1) was obtained. Attempted hydrogenation of **1** over palladium on carbon in ethanol failed and resulted in the complete isomerization into **4**.

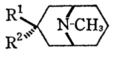


Scheme 1.

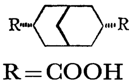
Several workers[4-7] concluded from analysis of the NMR patterns corresponding to the carbinyl proton in the bicyclo[3.3.1]nonan-3-ols (**10**, **11**, **13**), that in the β-ols the major conformer is of a double chair form but in the α-ols the cyclohexanol ring exists in a boat form as a more stable conformer. In the same way, the conformation of the cyclohexanol rings of the two epimers (**2** and **5**) were studied by analysis of the patterns of the carbinyl protons by the first order approximation. The coupling constants obtained are shown in Table 1 with the values of the analogous compounds. The values for the β-ol (**5**); $J_{3,2\beta}=11.4$ and $J_{3,2\alpha}=5.3$ Hz indicate that the cyclohexanol ring exists in a normal chair form with an equatorial hydroxyl group as compared with the other β-ols. The values obtained for α-ol (**2**), $J_{3,2\beta}=6.1$ and $J_{3,2\alpha}=1.1$ Hz, differing from the other α-ols in the boat form, indicate that the cyclohexanol ring takes a chair ar-



10a R=R¹=H, R²=OH
10b R=R²=H, R¹=OH
11a R=CH$_3$, R¹=H, R²=OH
11b R=CH$_3$, R¹=OH, R²=H
12a R=R¹=H, R²=COOCH$_3$
12b R=R²=H, R$_1$=COOCH$_3$



13a R¹=H, R²=OH
13b R¹=OH, R¹=H



14a R=COOH
14b R=COOCH$_3$
14c R=C(CH$_3$)$_2$OH

Formula 1.

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[13] For extensive literature survey see W. D. Horock, Jr., J. R. Sipe, III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).

[14] M. A. Eakin, J. Martin, W. Parker, C. Egan, and S. H. Graham, *Chem. Commun.*, **1969**, 737.

[15] J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, **32**, 1372 (1967).

TABLE 1. COUPLING CONSTANS OF H_3-H_2 IN THE BICYCLO[3.3.1]NONANE SYSTEMS

Compound	Substituent (s)	$J_{3,2\beta}$	$J_{3,2\alpha}$	Supposed Conformation	Reference
2	α	6.1	1.1	chair	this work
5	β	11.4	5.3	chair	this work
10a	α	6.2	10.0	boat	7
11a	α	6.6	9.0	boat	4
11b	β	11.4	6.6	chair	4
13a	α	4	11	boat	5
13b	β	9.8	6.9	chair	5
14a	α,α	7.1[a]	7.1[a]	boat-chair	11
14b	α,α	7.1[a]	7.1[a]	boat-chair	11
14c	α,α	6.0	12.0	boat-boat	11

a) Time-averaged values for the boat-chair equilibrium.

rangement with an axial hydroxyl group. It was reported[16] that in ring A of steroids where the ring is known to be in a regular chair form, the vicinal coupling constants are $J_{3,2\beta}\cong 10$ and $J_{3,2\alpha}=5.5\pm 1.0$ Hz for the axial carbinyl proton and $J_{3,2\beta}=J_{3,2\alpha}=2.0$—3.2 Hz for the equatorial carbinyl proton. If we take the above steroid system as a model, the chair form of the cyclohexanol ring of **2** might be supposed to undergo a considerable distortion[17] or make some contribution of the boat form to the conformational equilibrium, since flattening would increase one dihedral angle (between $H_{(3)}$ and $H_{(2)}$) and decrease the other from their initial values of 60°, which would lead to a somewhat smaller value for $J_{3,2\alpha}$ and a slightly larger value for $J_{3,2\beta}$.

The deduction that the cyclohexanol rings in **2** as well as **5** take chair conformations seems curious from the fact that the boat form is preferred in all α-ols (**10a**, **11a**, **13a**). To obtain information on the conformation, the NMR spectra of **2** and **5** were studied with NMR shift-reagent, $Eu(DPM)_3$, which complexes with a lone pair to induce shift mainly dependent on Eu–H distances.[13]

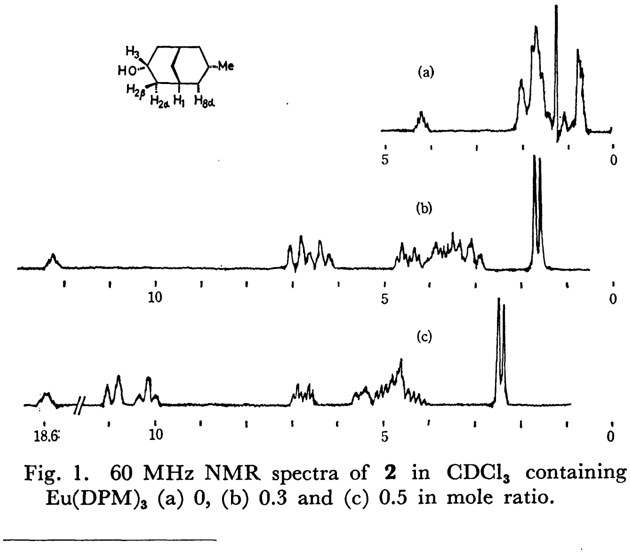
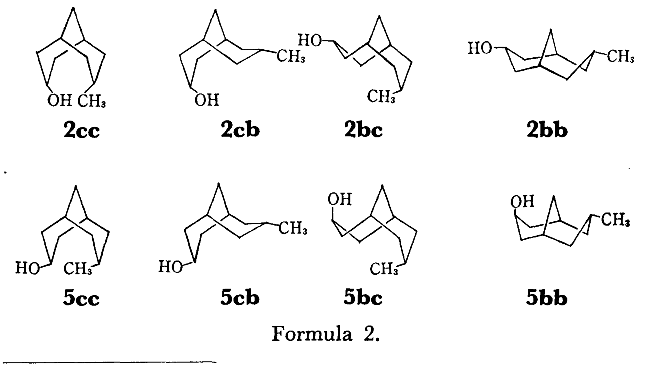


Fig. 1. 60 MHz NMR spectra of **2** in $CDCl_3$ containing $Eu(DPM)_3$ (a) 0, (b) 0.3 and (c) 0.5 in mole ratio.

NMR spectra of **2** before and after addition of 0.3 and 0.5 molar ratio of $Eu(DPM)_3$ are shown in Fig. 1. In spectrum 1(b), the one-proton signal at the lowest field (δ 12.3) is assignable to the carbinyl proton from chemical shift. On irradiation at this signal position, the doublet of triplets (2H) centered at δ 4.60 collapsed into a two-line multiplet, indicating that the signal is assignable to $H_{(2\beta)}$. However, the assignment of β-configuration mainly rested in the generality[18] that the extent of deshielding to the protons located vicinally to a hydroxyl group appears to be dependent upon the magnitude of the dihedral angle between the hydroxyl group and the proton under consideration when $Eu(DPM)_3$ was used as the shift-reagent. The two-line multiplet (2H) centered at δ 6.96 is assigned to $H_{(2\alpha)}$ from the spacing of 15 Hz which is included also in the signal of $H_{(2\beta)}$ and from the mutual decoupling experiments (although imperfect) with the $H_{(2\beta)}$. From these signals in the spectra 1(b) and 1(c), the following coupling constants were obtained; $J_{3,2\beta}=6.0$, $J_{3,2\alpha}<1.5$, $J_{2\alpha,2\beta}=15$, $J_{1,2\beta}=4.5$ Hz. They are reasonably coincident with those obtained earlier. The three-line multiplet (2H) centered at δ 6.44 (Fig. 1 (b)) is assigned to $H_{(8\alpha)}$ because the signal collapsed into a two-line multiplet upon irradiation at the point where maximum coalescence of the three-proton



Formula 2.

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[16] L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd Ed., Pergamon Press, Oxford (1969), p. 283.

[17] As a rough approximation the deviation ($\Delta\Phi$) from the normal value (60°) was calculated as 22.5°, using the relationship $J=J_0\cos^2\Phi-C$(Ref. 16, p. 281) provided that $J=3.0$ Hz at $\Phi=60°$(taking the value for the equatorial carbinyl proton as a model (see text)), $J=6.1$ Hz at $\Phi=60°-\Delta\Phi$, and $J=1.1$ Hz at $\Phi=60°+\Delta\Phi$ were adopted.

[18] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5737, 5739 (1970).

doublet (δ 1.70) of the methyl protons could be obtained. It should be noted that the signal due to $H_{(8\alpha)}$ is more shifted than that of $H_{(2\beta)}$ indicating that $H_{(8\alpha)}$ proton is situated in the proximity of the hydroxyl group; this requires the cyclohexanol ring to be in the chair form and the methylcyclohexane ring in the boat form (2cb). The observation that the methyl protons are shifted much less than the other protons at both concentrations of $Eu(DPM)_3$ (1(b) and 1(c) in Fig. 1) suggests that the methyl group is located farthest from the hydroxyl group; this requires the methyl cyclohexane ring to be in a boat conformation since the cyclohexanol ring exists in a chair form.

NMR spectra of the epimeric alcohol (**5**) before and after addition of $Eu(DPM)_3$ in molar ratios 0.3 and 0.5 are shown in Fig. 2; the decoupling experiments and the assignments were made on spectrum 2(c).

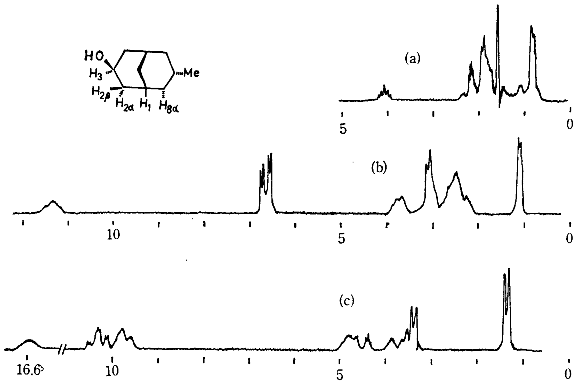

Fig. 2. 60 MHz NMR spectra of **5** in $CDCl_3$ containing $Eu(DPM)_3$ (a) 0, (b) 0.3 and (c) 0.5 in mole ratio.

From the change in pattern induced by the irradiation at the one-proton signal at δ 16.60 due to the carbinyl proton ($H_{(3)}$), the signals (each 2H) centered at δ 10.35 and 9.76 are assigned to $H_{(2\alpha)}$ and $H_{(2\beta)}$. Judging from these signals especially on the irradiation at the $H_{(1)}$ signal (the assignment is mentioned later), the following values are obtained; $J_{3,2\beta}=11$, $J_{3,2\alpha}=ca.$ 5, $J_{2\alpha,2\beta}=14$, $J_{1,2\beta}=3$ Hz. They indicate that the cyclohexanol ring is in a normal chair conformation with an equatorial hydroxyl group. In contrast to the case of **2**, the infiuence of the shift-reagent on the $H_{(8\alpha)}$ (tentatively assigned to the signal at δ 4.55) is much smaller. The smallest effect of the shift-reagent on the methyl protons implies that the methylcyclohexane ring takes a boat form since the cyclohexanol ring exists in the chair form.

Another assignable proton in **2** and **5** is the bridgehead proton ($H_{(1)}$) judging from the featureless broadening due to the six vicinal protons and from the decoupling experiments irradiated at the $H_{(2\beta)}$ signals. The signals have a half-height width of 18.1 Hz (δ5.5) in spectrum 1(c) for **2** and 18.5 Hz (δ4.8) in 2(c) for **5**.

The deduction that in **2** and **5** the methylcyclohexane ring exists in a boat conformation might be supported by the following fact. In the IR spectra of the bicyclo-[3.3.1]nonane systems which exist predominantly in a double chair conformation, the stretching and bending bands are known to appear in the abnormally higher-frequency region (near 2990 and 1490 cm^{-1}, respectively.)[19] Both **2** and **5** show no such absorption. This indicates the relief of strain due to the double chair form.

In consequence, the actual preferred conformer for **2** is the boat-chair form (**2cb**) with a considerable flattening of the cyclohexanol ring or with a slight contribution of the double boat form (**2bb**) to the equilibrium.[20] In the case of **5** the boat-chair form (**5cb**) is predominantly preferred.

Two 1,3-diaxial methyl-methylene interactions may be estimated roughly to be 2×3.7 kcal/mol and two 1,3-diaxial hydroxyl-methylene interactions to be 2× 2.4 kcal/mol.[21] This is why the methylcyclohexane ring (**2cb**), and not the cyclohexanol ring (**2bc**), takes the boat conformation in order to avoid the repulsion in the double chair form (**2cc**). A similar deduction is derived for **5** since the two 1,3-diaxial hydrogen-methylene interactions are estimated to be 2×0.85 kcal/mol.

The $\Delta G°$ values for the equilibration between **10a** and **10b**,[6] and **12a** and **12b**[9] have been reported to be −2.5 and −2.7 kcal/mol, respectively. Since the β-isomer exists predominantly in the double chair form and the α-isomer in the chair-boat form and the substituents in both cases have equatorial arrangement, the $\Delta G°$ values can be ascribed to the energy difference of the structural change between the double chair and chair-boat forms. It is thus interesting that in **2** the double boat conformation **2bb** is not preferred over **2cb** although the former does not possess the two 1,3-diaxial methylene-hydroxyl interactions which are present in the latter.

The $\Delta G°$ value for the equilibration between **2** and **5** was found to be −2.18 kcal/mol by the equilibration starting from either **2** or **5** with aluminum isopropoxide in isopropyl alcohol at 110°C. Since the cyclohexanol rings in **2** and **5** exist in the chair form, contrary to reported cases, this value can be supposed to be the free energy difference dependent on the axial-equatorial nature of the hydroxyl group. Since two 1,3-diaxial hydroxyl-methylene interactions may be estimated to be 2×2.4 kcal/mol or somewhat smaller and two hydrogen-methylene interactions as 2×0.85 kcal/mol,[21] the energy difference would be about 3.1 kcal/mol. Agreement with the experimental value is considered to be reasonably satisfactory.

Experimental

All the melting and boiling points are uncorrected. IR spectra were recorded on a Shimadzu IR-27C spectrometer, and NMR spectra were obtained with a JEOL C-60H spectrometer in $CDCl_3$ and CCl_4 solutions using tetramethyl-

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[19] G. Eglinton, J. Martin, and W. Parker, *J. Chem. Soc.*, **1965**, 1243.

[20] Attempts to obtain NMR spectra of the fixed conformations of **2** and **5** at lower temperature were unsuccessful due to the crystallization of the substrates in carbon disulfide as well as Freon 11 solution at −50°C.

[21] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York (1965), p. 50.

silane as an internal standard. Mass spectra were recorded with a Hitachi RMS-4 mass spectrometer with a nominal ionizing energy of 70 eV and a source temperature of 150°C. Glc analyses and separation were carried out on a Shimadzu GC-4APT using a 3 mm × 3 m column with 15% polyethylene glycol on Chromosorb W (60/80 mesh) operating at 150°C with helium flow rate 40 m*l*/min. Microanalyses were carried out by Mrs. K. Fujimoto.

7-Methylenebicyclo[3.3.1]nonan-3-one (**1**),12) 7-methylenebicyclo[3.3.1]nonan-3α-ol (**7**)14) and -3β-ol14) were prepared according to the published methods. Tris(dipivalomethanato)europoium(III), Eu(DPM)$_3$, was prepared in a similar manner to the method of Eisentraut22); mp 189.5—190°C (lit,23) mp 190—191°C).

*Hydrogenation of **1** over Platinum Oxide in Acetic Acid.* A solution of **1** (300 mg) in acetic acid (20 m*l*) was hydrogenated over platinum oxide (70 mg) for 20 hr. The catalyst was removed by filtration and the filtrate was neutralized with aqueous sodium bicarbonate solution and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. The residue was purified by sublimation to give 293 mg (95%) of **2**, mp 101—102°C. Found: C, 77.70; H, 11.99%. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76%. IR (KBr): 3252, 2903, 1455, 1368, 1119 cm^{-1}; IR (CCl_4): 2908, 1461 cm^{-1}. NMR ($CDCl_3$): δ 0.85 (d, CH_3), 1.34 (s, OH), 4.15 (m, $H_{(3)}$). MS: *m/e* 154 (M^+).

*Hydrogenation of **7** over Platinum Oxide in Acetic Acid.* Platinum oxide (8 mg) in 3 m*l* of acetic acid was added to a solution of **7** (50 mg) in 3 m*l* of acetic acid, and the mixture was stirred under an atmosphere of hydrogen for 24 hr. After the same work-up as described above, 46 mg (92%) of **2** was obtained.

*Hydrogenation of **8** over Platinum Oxide in Acetic Acid.* A sample of **8** (45 mg) in acetic acid (6 m*l*) was hydrogenated for 16 hr over 10 mg of platinum oxide. After the usual work-up, sublimation of the residue *in vacuo* afforded 43 mg (95%) of **5**. Found: C, 77.97; H, 11.92%. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76%. IR (KBr): 3274, 2923, 1462, 1375, 1059 cm^{-1}; IR (CCl_4): 2925, 1466 cm^{-1}. NMR($CDCl_3$): δ 0.84 (d, CH_3), 1.59 (s, OH), 3.97 (m, $H_{(3)}$). MS: *m/e* 154 (M^+).

*Oxidation of **2** and **5** into **3**.* To a solution of a complex prepared from chromic trioxide (600 mg) and pyridine (950 mg) in 20 m*l* of dichloromethane was added 100 mg of **2** in 3 m*l* of dichloromethane. The mixture was treated as described by Ratcliffe.24) After the usual work-up, sublimation gave the ketone (**3**), mp 42.5—43.5°C in 90% yield. The same treatment of **5** also afforded **3** in almost the same yield. Found: C, 78.87; H, 10.77%. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59%. IR(KBr): 1704, 1379, 1354, 1087 cm^{-1}. MS: *m/e* 152 (M^+).

*Hydrogenation of **1** over Platinum Oxide in Ethyl Acetate.* A solution of **1** (100 mg) in 11 m*l* of ethyl acetate was hydrogenated for 2 days over 20 mg of platinum oxide. Removal of the catalyst and evaporation of the solvent gave a mixture of **3** and **4** in the ratio 4.5 : 1. Prolonged reaction (4 days) gave **3** exclusively. Hydrogenation of **1** (4.9 g) over a small amount of platinum oxide (100 mg) for 4 days gave a mixture of **3** and **4** in the ratio 3 : 2. Isolation of **3** and **4** was carried out by preparative glc, followed by sublimation and distillation, respectively. **3** was also isolated from the mixture by recrystallization three times from methanol at −65°C, mp 42.5—43.5°C. Ketone (**3**) was identical with the one obtained above by oxidation of **2** and **5** (spectroscopic data and mixed mp).

The analytical sample of **4**, bp 106—107°C/11 mmHg, showed single peak in glc analysis. Found: C, 79.69; H, 9.35%. Calcd for $C_{10}H_{14}O$: C, 79.69; H, 9.35%. IR (liquid): 3010, 1713, 1376, 1358 cm^{-1}. NMR(CCl_4): δ 1.64 (s, CH_3), 5.41 (d, =C–H). MS: *m/e* 150 (M^+).

*Isomerization of **1**.* A solution of **1** (100 mg) in 8 m*l* of ethanol was stirred overnight over 20 mg of 5% palladium on charcoal under hydrogen atmosphere. Removal of the catalyst and evaporation of the solvent gave **4** in 100% conversion. A solution of **1** (100 mg) in 5 m*l* of ethanol was refluxed under vigorous stirring for 24 hr over 20 mg of platinum oxide under nitrogen atmosphere. After removal of the catalyst and evaporation of the solvent the residue was found to consist of 33% of **4** and 67% of **1** by glc analysis. A similar treatment over palladium on charcoal instead of platinum oxide gave no isomerization product and led to the recovery of the starting material.

*Hydrogenation of **4**.* A solution of 60 mg of **4** in 5 m*l* of ethyl acetate was hydrogenated for 80 hr over 10 mg of platinum oxide. The usual work-up quantitatively gave **3** as the sole product.

*Lithium Aluminum Hydride Reduction of **3**.* A solution of **3** (98 mg) in 6 m*l* of ether was added dropwise to a slurry of 32 mg of lithium aluminum hydride in 10 m*l* of ether under stirring. The reaction mixture was refluxed for 6 hr and then dilute hydrochloric acid was added to destroy the excess hydride. The ethereal layer was dried (Na_2SO_4) and evaporated. The residue was found to consist of **2** and **5** in the ratio 4 : 1 by glc analysis.

Equilibration. Reagents and solvents for equilibration were prepared according to the method described by Eliel.25) The reaction was carried out in sealed tubes because of sublimation of the substrates.

Equilibration was performed on each 10 mg sample of the alcohols in a mixture of 12 mg of aluminum isopropoxide, 2 m*l* of acetone and 0.5 m*l* of isopropyl alcohol at 110°C. The reaction was quenched by pouring the mixture into 1 m*l* of 0.7 N hydrochloric acid and extracted with petroleum ether (bp 40—60°C). The extracts were dried (Na_2SO_4) and used for glc analysis which showed the equilibrium was established after 20 days. The results are summarized in Table 2.

Table 2. Equilibration between **2** and **5**

Run	Starting substrate	Time (days)	Composition **2**	: **5**
1	2	7	9.1	90.9
2	2	20	5.4	94.6
3	5	7	2.0	98.0
4	5	23	5.3	94.7

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