

TABLE IV
 CHARACTERIZATION OF THE BICYCLIC ANIONS

Adduct	Mp, °C	λ_{\max} , m μ	Calcd, %			Found, %		
			C	H	N	C	H	N
1 ^a	171-172	510 ^b	45.35	5.85	16.27	45.40	5.78	16.25
2 ^c	190-191	500 ^b	61.82	6.15	10.68	61.72	6.18	10.80
3	157-158	515 ^b	46.63	5.74	14.50	46.89	6.00	14.80
4	152-153	506 ^d	49.27	6.57	13.52	49.46	6.33	13.38
5	144-160 ^e	507 ^b	46.63	5.74	14.50	46.76	5.62	14.22
6	180-181	504 ^d	48.24	5.57	14.06	48.44	5.86	13.86
7	147-148	504 ^d	48.64	6.35	12.60	48.60	6.43	12.50
8	157-164	504 ^d	48.86	5.92	12.66	48.58	6.00	12.90
9	119-122	500 ^b	46.71	5.78	11.47	46.84	5.83	11.36
10	146-151 ^e	374 ^d	53.76	6.65	13.20	53.91	6.80	13.24
11	126-127	382 ^d	51.27	6.03	11.96	50.93	5.92	12.09
12	118-119	375 ^d	50.30	6.23	8.38	50.55	6.35	8.33
13	140-150 ^e	372 ^d	50.39	6.49	11.76	50.40	6.59	11.54

^a Reference 3. ^b In acetone. ^c Reference 4. ^d In methanol. ^e Melts with decomposition.

A typical example is outlined below. The elemental analyses, melting points, and visible maxima of 1-13 are summarized in Table IV.

1,3-Dicarbomethoxyacetone-1,3,5-trinitrobenzene (9).—A mixture of 1.3 ml of 1,3-dicarbomethoxyacetone and 2.13 g (0.01 mol) of trinitrobenzene was warmed until the aromatic compound dissolved, and *ca.* 3 ml of triethylamine was then added. The greenish, tarlike mixture was kept at room temperature for 4 hr and 5 ml of methanol was added. The resultant slurry was added to 75 ml of anhydrous ether and the mixture was cooled. The crude product which precipitated was filtered and recrystallized from a 1:1 ether-methanol mixture to give a 30% yield of brilliant red crystals, mp 119-122°.

Registry No.—1, 12379-55-4; 2,12 379-64-5; 3-6, mixture, 12379-56-5; 7, 12379-59-8; 8, 12379-58-7; 9,

12379-61-2; 10, 12379-60-1; 11, 12379-62-3; 12, 12379-63-4; 13, 12379-57-6.

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Conformational Equilibria for 2- and 3-Bicyclo[3.3.1]nonanols¹

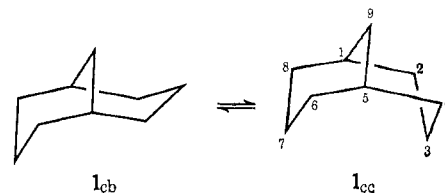
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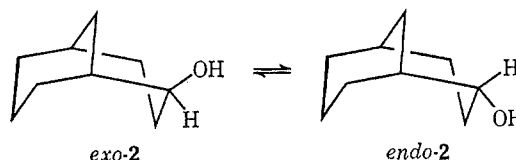
Equilibration of either the *exo*- or *endo*-3-bicyclo[3.3.1]nonanols with aluminum isopropoxide in isopropyl alcohol at 94° gave 96.9% *exo* isomer. The ΔG° of -2.5 kcal/mol obtained is a reasonable approximation of the energy difference between the chair-boat and double-chair conformers of bicyclo[3.3.1]nonane. Equilibration of either of the two isomers of 2-bicyclo[3.3.1]nonanol under the same conditions gave 68.7% *endo* isomer (equatorial hydroxyl). In this protic solvent, $\Delta G^\circ_{\text{OH}} = -0.56$ kcal/mol. Equilibration over Raney nickel in cyclohexane gives a $\Delta G^\circ_{\text{OH}}$ of -0.25 kcal/mol for an aprotic solvent.

Bicyclo[3.3.1]nonane provides an interesting vehicle for the study of conformational effects. Thus it has been established,² contrary to most expectations,³ that the molecule adopts preferentially the double-chair rather than the chair-boat conformation. No estimate of the energy difference between these two conformations was available when the study reported here was made.⁴ X-Ray studies² showed that the ring distorts readily parallel to the plane of symmetry through C₃, C₇, and C₉, but is resistant to distortions which destroy



this as a symmetry element. Little has been done to ascertain the influence of these ring distortions on the conformational preferences of ring substituents.

Equilibration of 2-Bicyclo[3.3.1]nonanols.—The two epimeric 2-bicyclo[3.3.1]nonanols, *exo*-2 and *endo*-2,



(1) The authors are pleased to make acknowledgment to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. A preliminary account of this work was given at the Northwest Regional Meeting of the American Chemical Society, Richland, Wash., June 1967.

(2) M. Dobler and J. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); W. A. C. Brown, J. Martin, and G. A. Sim *J. Chem. Soc.* 1844 (1965).

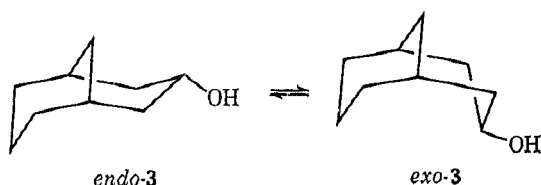
(3) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 295-296.

(4) See, however, R. A. Appleton, C. Egan, J. M. Evans, S. H. Graham, and J. Dixon, *J. Chem. Soc., C*, 1110 (1968).

were prepared according to known procedures.⁵⁻⁷ Pure samples were collected by preparative gas chromatography, and these had physical and spectral properties in excellent agreement with published values. The equilibrium mixtures were analyzed directly by glpc. Equilibration over aluminum isopropoxide in isopropyl alcohol at 94° was carried out from both pure epimers. The equilibrium mixture contained 31.0% *exo*-2 and 69.0% *endo*-2. Equilibration over Raney nickel catalyst in isopropyl alcohol⁸ gave an equilibrium mixture containing 31.3% *exo*-2 and 68.7% *endo*-2. Thus in isopropyl alcohol $\Delta G^0_{OH} = -0.56$ kcal/mol. Our value is in excellent agreement with the value of -0.559 kcal/mol obtained by Baggeley, *et al.*,⁹ and published after our work was nearly completed.

The equilibration of *exo*-2 and *endo*-2 was also carried out in cyclohexane using Raney nickel as catalyst.⁸ The equilibrium mixture contained 40.5% *exo*-2 and 59.5% *endo*-2 with $K = 1.47$ and $\Delta G^0_{OH} = -0.25$ kcal/mol.

Equilibration of 3-Bicyclo[3.3.1]nonanols.—Both the *exo*- and *endo*-3-bicyclo[3.3.1]nonanols (**3**) were prepared by established procedures⁵ and purified by pre-



parative gas chromatography. Our sample of *exo*-3 showed a high-frequency methylene stretch at 2968 ± 2 cm^{-1} , whereas Hartmann and Gräfe¹⁰ report 2980 cm^{-1} . However, our sample has an nmr spectrum which duplicates that reproduced in Schaefer's paper.⁵ Direct glpc analysis of the isomers of **3** was not possible; so mixtures were converted into the acetates, which were analyzed *via* glpc. Check runs on known mixtures showed that the method was reliable and accurate to at least 1 part in 100.

Each of the epimers was equilibrated over aluminum isopropoxide according to the procedure of Eliel and Ro.¹¹ When equilibration was made in boiling isopropyl alcohol, the mixture obtained from *endo*-3 consisted of 4.3% *endo*-3 and 95.7% *exo*-3, while the mixture from *exo*-3 contained 3.6% *endo*-3. Difficulty was experienced with sublimation of the alcohols from the reaction mixture; so all later runs were made in sealed tubes. Duplicate runs at 94.1° starting with either epimer gave 3.1% *endo*-3 and 96.9% *exo*-3. Thus the equilibrium constant for the *endo*-*exo* conversion is 31.3 and $\Delta G^0_{94} = -2.51$ kcal/mol. An attempt to repeat the studies using Raney nickel gave only 2-bicyclo[3.3.1]nonanone.

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

(6) R. A. Appleton, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 805 (1967).

(7) E. N. Marvell, G. J. Gleicher, D. Sturmer, and K. Salisbury, *J. Org. Chem.*, **33**, 3393 (1968).

(8) E. L. Eliel and S. M. Schroeter, *J. Amer. Chem. Soc.*, **87**, 5031 (1965).

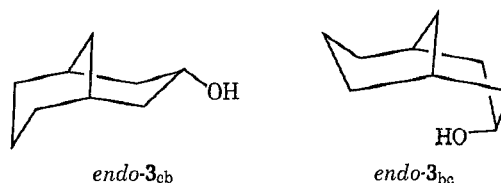
(9) K. H. Baggeley, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 299 (1967).

(10) M. Hartmann and U. Gräfe, *Angew. Chem.*, 305 (1967).

(11) E. L. Eliel and R. S. Ro, *J. Amer. Chem. Soc.*, **79**, 5992 (1957).

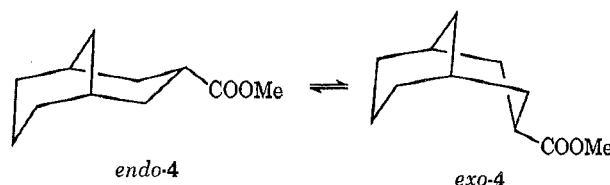
Discussion

The ΔG^0 for the *endo*-3 to *exo*-3 equilibrium represents a reasonable value for the 1_{cb} - 1_{cc} equilibrium. The ΔG^0 values for the substituted isomers and the unsubstituted conformers will correspond accurately only when (a) the *exo* isomer exists predominantly in the double chair and the *endo* in the chair-boat conformations; and (b) the substituents alter the energies of the conformations in parallel fashion. Both conditions appear to be satisfied here. The double-chair conformation for *exo*-3 is supported by the spectral data.¹² While a double-chair conformation has been suggested¹³ for *endo*-3, the case for the chair-boat conformation has been argued effectively^{4,12} and will not be repeated here. There are two possible chair-boat conformers for *endo*-3, *endo*-3_{bo} and *endo*-3_{cb}. The



former is excluded because it possesses two 1,3-diaxial methylene-hydroxyl interactions not present in the latter.¹⁴ Thus the first condition is satisfied. Since the hydroxyl group is effectively in an equatorial position in each isomer, the second condition is also satisfied.

Our conclusion that the ΔG^0 for the 1_{cb} - 1_{cc} equilibrium is 2.5 kcal/mol (at 94°) is supported by the report⁴ that ΔG^0_{25} for the *endo*-4-*exo*-4 equilibrium is 2.7 kcal/mol. That the ΔG^0 value is thus inde-



pendent of the nature of the substituent indicates clearly that the energy difference is that for the skeletal change only. If 1_{cb} and 1_{cc} are assumed to be of equal entropy except for that due to the higher symmetry of 1_{cc} , the $\Delta H = 2.9$ - 3.2 kcal/mol can be compared with a calculated potential-energy difference for the two conformers. Using a modified Wiberg program,^{16,17} we have calculated⁷ that this value is 3.7 kcal/mol. The agreement is reasonably satisfactory.

The total strain energy for 1_{cc} compared with chair cyclohexane as a strain-free model can now be estimated. The lateral rigidity of the bicyclo[3.3.1]nonane ring² ensures that 1_{cb} will possess a C_{2v} boat form. Thus the strain energy of 1_{cb} is the sum of a chair cyclohexane (0.0 kcal/mol) and a C_{2v} boat cyclohexane (6.9 kcal/mol).¹⁸ Since 1_{cc} has *ca.* 2.9 kcal/

(12) W. O. K. Macrosson, J. Martin, and W. Parker, *Tetrahedron Lett.*, 2589 (1966).

(13) C.-Y. Chen and R. J. W. Le Fevre, *ibid.*, 737 (1965).

(14) For a cyclohexane ring a methyl-hydroxyl diaxial interaction is unfavorable by 2.4 kcal/mol,¹⁵ and two somewhat smaller but similar interactions seems quite sufficient to eliminate *endo*-3_{bo}.

(15) E. L. Eliel and H. Haubenstock, *J. Org. Chem.*, **26**, 3504 (1961).

(16) K. B. Wiberg, *J. Amer. Chem. Soc.*, **87**, 1070 (1965).

(17) G. J. Gleicher and P. von R. Schleyer, *ibid.*, **89**, 582 (1967).

(18) J. B. Kendrickson, *ibid.*, **83**, 4537 (1961).

mol less strain than 1_{ob} , the total strain energy for 1_{oc} must be close to 4.0 kcal/mol. Clearly the calculated¹⁷ value of 11.7 kcal/mol is much too large.

Our results for the *endo-2-exo-2* equilibrium provide two ΔG^0_{OH} values, 0.25 kcal/mol in an aprotic solvent and 0.56 kcal/mol for protic solvents. Two values for ΔG^0_{OH} have been found for cyclohexane,⁸ 0.6–0.7 for aprotic media and 0.90 for protic media. In view of the general uncertainties associated with conformational ΔG^0 values in general and for the hydroxyl group particularly,⁸ the values for the bicyclic molecule can be said to be about half of those found for cyclohexane. This relation can be readily accounted for, and it suggests that the distortions of a normal cyclohexane ring present in 1_{oc} do not materially influence the ΔG^0 (see below).

The equatorial (*endo*) position at C_2 in 1_{oc} differs from a normal equatorial position in a cyclohexane ring by having a diaxial interaction with the *endo* hydrogen at C_3 .⁷ Assuming that 1,3-diaxial interactions are additive, the *exo* position at C_2 has two of these while the *endo* has one. For cyclohexane the axial position has two and the equatorial none. Hence the ΔG^0 for C_3 on the bicyclic system should be half that for a cyclohexane ΔG^0 . The experimental results are in accord with this simple analysis. It must be noted, however, that the $C_1-C_2-C_3$ angle in the bicyclic ring is *ca.* 114°, which tilts the *exo* bond outward from the threefold axis of a cyclohexane ring by about 9°. This distortion, which is about one-third of that required to produce a planar cyclohexane ring, would be expected to reduce the interactions in the *exo* position, and hence to reduce the ΔG^0 at C_2 to considerably less than half the normal value. The results indicate that this distortion has little if any influence on the relative ΔG^0 values. We attribute this to the distortions made in the more flexible cyclohexane ring to minimize axial interactions, which reduce the normal ΔG^0 for cyclohexane in a manner not accessible to the more rigid bicyclic system.

The computed geometry⁷ and the van der Waals parametrization of Hill¹⁹ were used to calculate the nonbonded interaction energy difference for *exo-2* and *endo-2*. The calculated ΔG^0 of 0.1 kcal/mol treats the hydroxyl as a spherical oxygen only and ignores the hydrogen. This value, which would be expected to equate more nearly to the ΔG^0 in an aprotic solvent, is in reasonable agreement with the experimental value of 0.25 kcal/mol.

Experimental Section

***exo-2*-Bicyclo[3.3.1]nonanol (*exo-2*).**—2-Bicyclo[3.3.1]nonen-9-one²⁰ (20.0 g, 0.15 mol) was dissolved in 200 ml of diethylene glycol containing 15 ml (0.31 mol) of 99% hydrazine hydrate and 14 g of potassium hydroxide. The mixture was heated slowly to 200° under nitrogen and heating was continued until no further water collected in the Dean-Stark trap (6–8 hr). The mixture was cooled, diluted with ice-water, and extracted with pentane. Material which had sublimed into the condenser was washed out with pentane, the combined pentane solutions were dried ($MgSO_4$), and the solvent was removed by evaporation to give 14.2 g (79%) of white solid. A sample purified by sublimation melted at 93–96° (lit.⁵ mp 96–97°).

The above olefin was converted into *exo-2,3*-epoxybicyclo[3.3.1]nonane by the method of Payne.²¹ A solution containing 1 equiv of bicyclo[3.3.1]nonene, 1 equiv of benzonitrile, a 50% molar excess of 30% hydrogen peroxide, and *ca.* 2 molar equiv of potassium bicarbonate in methanol was stirred at room temperature for 48 hr. Water was added and the organic products were taken up in pentane and dried ($MgSO_4$). The solvent was removed *in vacuo*, and glpc analysis (15 ft \times 1/4 in. 5% FFAP on Chromosorb G at 118°) showed the product to consist of a mixture of epoxide and unreacted benzonitrile and olefin. This was separated *via* preparative thin layer chromatography (Merck PF₂₅₄ silica gel, benzene; olefin R_f 0.7, benzonitrile R_f 0.4, epoxide R_f 0.25) and the epoxide was purified by sublimation *in vacuo*, mp 182–183°, yield 25–30%.

Anal. Calculated for $C_9H_{14}O$: C, 78.22; H, 10.21. Found: C, 78.04; H, 9.98.

A mixture of 13 g (0.094 mol) of crude *exo-2,3*-epoxybicyclo[3.3.1]nonane and 27 g (0.074 mol) of lithium aluminum hydride in 800 ml of tetrahydrofuran was heated at 50° for 24 hr. Excess hydride was destroyed by careful addition of water, and the organic layer was decanted. Precipitated solids were washed with ether and the extracts were combined with the decanted solution. The solvent was removed *in vacuo* and the crude alcohol was purified by sublimation: mp 175–178° (lit.⁵ mp 176–177°); ir (CCl_4) 3600, 3400, 2980 (sh), 1480, and 1030 cm^{-1} ; nmr (CCl_4) δ 3.80 (m, 1 H), 3.20 (s, 1 H), and 0.9–2.4 (m, 14 H). Analysis *via* glpc (12 ft \times 0.125 in. 5% FFAP on Chromosorb G at 118°) showed 9.9% *endo* epimer present as an impurity. Samples for use in the equilibration were purified by preparative gas chromatography.

A *p*-nitrobenzoate was prepared by heating 50 mg of the alcohol with a 10% excess of *p*-nitrobenzoyl chloride in 1 ml of pyridine at 80° for 3 hr. Water (5 ml) was added and the mixture was extracted with ether. The ether extracts were washed with sodium bicarbonate solution and dried over sodium sulfate, and the solvent was removed by distillation. The product was recrystallized from hexane, mp 110–112° (lit.⁵ mp 111–112°).

***endo-2*-Bicyclo[3.3.1]nonanol (*endo-2*).**—A solution of 2-bicyclo[3.3.1]nonanone²² (4.5 g, 33 mmol) in 16 ml of methanol was added dropwise to a solution of 2.45 g (64 mmol) of sodium borohydride in 32 ml of methanol. The reaction mixture was kept at 15° until addition had been completed and was then stirred overnight at room temperature. Excess hydride was destroyed, 700 ml of water was added, and the solution was extracted with pentane. The pentane extracts were dried (K_2CO_3) and the solvent was removed. The product was purified by sublimation, mp 178–182° (lit.⁵ mp 177–178°), yield 3.6 g (80%). Analysis by glpc (12 ft \times 0.125 in. 5% FFAP on Chromosorb G at 120°) indicated the presence of 2% *exo-2* as an impurity. Samples for equilibration were purified by preparative gas chromatography.

A *p*-nitrobenzoate was prepared as described under *exo-2*, mp 103–105° (lit.⁵ mp 101–102°).

***exo-3*-Bicyclo[3.3.1]nonanol (*exo-3*).**—This alcohol was prepared on a 0.25-mol scale from 2-bicyclo[3.3.1]nonene according to the procedure of Schaefer, *et al.*⁵ The crude product was purified by sublimation to give a white solid, mp 118–125°, in 50% yield. Analysis on a 100-ft capillary column (MBMA at 128°) showed 83% *exo-3*. This was further purified by preparative glpc (15 ft \times 0.375 in. Carbowax 20M on firebrick) to give a solid, mp 100–102° (lit.⁵ mp 100–101°), which analyzed as better than 99% *exo-3*. The nmr spectrum was identical with that reproduced in the literature.⁵

A *p*-nitrobenzoate was prepared as described for *exo-2*, mp 148–151° (lit.¹⁰ mp 150–151°).

***endo-3*-Bicyclo[3.3.1]nonanol (*endo-3*).**—To a solution of 3.5 g (25 mmol) of *exo-3* in 30 ml of anhydrous pyridine was added over a 2-hr period a mixture of 7.5 g (75 mmol) of chromium trioxide in 75 ml of anhydrous pyridine. The reaction mixture was stirred at 45° for 48 hr. A solution containing 9 g of sodium bisulfite in 25 ml of water was then added to the reaction mixture, and the solution was acidified with concentrated hydrochloric acid. The product was extracted with pentane, and the extracts were washed with water and dried ($MgSO_4$). Removal of the solvent by distillation gave 2.7 g (78%) of crude ketone. Sublimation gave 2.5 g of product, mp 172–177° (lit.⁵ mp 170–176°).

The above product was reduced with sodium borohydride according to the procedure of Schaefer, *et al.*⁵ Compound *endo-3*

(19) T. L. Hill, *J. Chem. Phys.* **16**, 399 (1948).

(20) S. Brewis and P. R. Hughes, *Chem. Commun.*, **6** (1966). We are deeply indebted to Dr. S. Brewis for a generous gift of this compound.

(21) G. B. Payne, *Tetrahedron*, **18**, 763 (1962).

(22) E. N. Marvell, D. Sturmer, and C. Rowell, *ibid.*, **22**, 861 (1966).

was obtained in 71% yield after purification by sublimation, mp 120–123° (lit.⁵ mp 121.5–124°). The nmr spectrum is in good agreement with that published.⁵

A *p*-nitrobenzoate was prepared according to the procedure given under *endo*-2, mp 101–103° (lit.¹⁰ mp 106–107°).

3-Bicyclo[3.3.1]nonyl Acetates.—For the glpc analysis the *exo*- and *endo*-3 mixtures were converted into the acetates. The alcohol mixture (ca. 100 mg) was mixed with 20 mg of anhydrous sodium acetate and 200 mg of acetic anhydride and the reaction mixture was heated for 2 hr at 100°. Ice (5 g) was added to the mixture and the product was taken up in pentane. The solution was dried (MgSO₄) and concentrated. Analysis was made *via* glpc as described below. Four independent runs on a sample containing 5.9% *endo*-3 and 94.1% *exo*-3 by weight gave 5.5:94.5, 5.6:94.4, 5.7:94.3, and 5.7:94.3%.

***exo*-3-Bicyclo[3.3.1]nonyl Acetate.**—A sample of pure *exo*-3 was acetylated as described above. The acetate was recovered by removal of the pentane: ir (neat) 1730, 1360, 1240, 1090 and 1030 cm⁻¹; nmr (CCl₄) δ 5.4 (m), 1.95 (s), and 0.8–2.4 (m).

Anal. Calcd for C₁₁H₁₆O₂: C, 72.49; H, 9.95. Found: C, 72.70; H, 10.06.

***endo*-3-Bicyclo[3.3.1]nonyl Acetate.**—A sample of the *endo* acetate prepared as above showed ir (neat) 1735, 1370, 1240, 1080, and 1010 cm⁻¹; nmr (CCl₄) δ 4.9 (m) and 0.7–2.5 (m).

Anal. Calcd for C₁₁H₁₆O₂: C, 72.49; H, 9.95. Found: C, 72.57; H, 10.06.

Equilibration.—Those equilibrations using Raney nickel as a catalyst used solvents and catalyst prepared as described by Eliel and Schroeter.⁸ A solution containing ca. 100 mg of the appropriate alcohol in 2–3 ml of solvent was mixed, with the catalyst (1–3 g) and sealed in a glass tube. The tube was suspended in a constant-temperature bath until equilibration (as determined from a series of check samples) was complete. The reaction was terminated by removal of the sample from the bath and after opening of the tube by removal of the catalyst by filtration. The catalyst was washed thoroughly and the solvent was removed by distillation. Analysis was made by glpc, and in most cases at least two runs were made from each side of the equilibrium. In the case of the 3-bicyclo[3.3.1]nonanols, the crude mixture was converted into the acetates prior to analysis as described above.

Reagents and solvents for equilibrations using aluminum isopropoxide were prepared as described by Eliel and Schroeter.⁸ Equilibrations were carried out on 100 mg of the alcohol with 110 mg of aluminum isopropoxide in 1–2 ml of isopropyl alcohol

containing 10–20 μl of acetone. A sealed-tube technique was used as described above. After equilibration had been completed, the contents of the reaction tube were poured into 5 ml of 0.7 *N* hydrochloric acid and the product was taken up in pentane. The pentane solution was dried (K₂CO₃) and used for analysis.

Analyses.—All analyses were carried out on an Aerograph 204B equipped with flame ionization detector and an L & N type W recorder with a Disc integrator. Mixtures of *exo*- and *endo*-2 were analyzed directly using a 12 ft × 0.125 in. 5% FFAP on Chromosorb G column at 125°. The *exo*- and *endo*-3 were converted into the acetates as described above and analyzed on a 100-ft capillary column with MBMA as a liquid phase at 125°. Peak areas indicated by the Disc integrator were checked by counting squares on the graph. All analyses were made in duplicate and the value reported is an average of the two (Table I).

TABLE I
RESULTS OF EQUILIBRATION STUDIES

Run	Reactant	Catalyst	Solvent	Time, days	Equilibrium mixture, <i>exo/endo</i>
1	<i>endo</i> -3	Al- <i>i</i> -PrO	<i>i</i> -PrOH	20	96.8:3.2
2	<i>endo</i> -3	Al- <i>i</i> -PrO	<i>i</i> -PrOH	20	96.9:3.1
3	<i>exo</i> -3	Al- <i>i</i> -PrO	<i>i</i> -PrOH	20	97.1:2.9
4	<i>exo</i> -3	Al- <i>i</i> -PrO	<i>i</i> -PrOH	23	96.7:3.4
5	<i>exo</i> -2	Al- <i>i</i> -PrO	<i>i</i> -PrOH	20	30.8:69.2
6	<i>endo</i> -2	Al- <i>i</i> -PrO	<i>i</i> -PrOH	20	31.3:68.7
7	<i>exo</i> -2	Raney Ni	<i>i</i> -PrOH	8	32.1:67.9
8	<i>endo</i> -2	Raney Ni	<i>i</i> -PrOH	8	31.2:68.8
9	<i>exo</i> -2	Raney Ni	C ₆ H ₁₂ ^a	10	41.0:59.0
10	<i>exo</i> -2	Raney Ni	C ₆ H ₁₂	10	41.0:59.0
11	<i>exo</i> -2	Raney Ni	C ₆ H ₁₂	10	39.6:60.4
12	<i>endo</i> -2	Raney Ni	C ₆ H ₁₂	10	42.0:58.0
13	<i>endo</i> -2	Raney Ni	C ₆ H ₁₂	10	39.8:60.2
14	<i>b</i>	Raney Ni	<i>i</i> -PrOH	2	30.6:69.4
15	<i>b</i>	Raney Ni	C ₆ H ₁₂	3.5	32.0:68.0

^a Cyclohexane. ^b 2-Bicyclo[3.3.1]nonanone.

Registry No.—*exo*-2, 22485-97-8; *endo*-2, 10036-25-6; *exo*-3, 10036-10-9; *endo*-3, 10036-08-5.

Synthesis of Bicyclo[3.3.1]nonanes. Products of the Friedel-Crafts Reaction of 3-(3-Cyclohexen-1-yl)propionyl Chloride¹

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A series of bicyclo[3.3.1]nonane derivatives can be prepared by a Friedel-Crafts reaction of 3-(3-cyclohexen-1-yl)propionyl chloride (2) under various conditions. Stannic chloride in chloroform gives 7-bicyclo[3.3.1]nonen-2-one (3) and 8-chloro-2-bicyclo[3.3.1]nonanone (4). Aluminum chloride in 1,2-dichloroethane leads to 6-chloro-2-bicyclo[3.3.1]nonanone (7), which can be converted into 6-bicyclo[3.3.1]nonen-2-one (8). With aluminum chloride in boiling cyclohexane, 2 gives 2-bicyclo[3.3.1]nonanone (6). Finally, 3-(3-cyclohexen-1-yl)propionic acid (1) gives 2,3,4,5,6,7-hexahydro-1-indenone (9) when treated with polyphosphoric acid.

Interest in the bicyclo[3.3.1]nonane ring system has been revived recently, in part because it is of importance in the synthesis of some complex natural products,⁴ and in part because it presents an interesting skeleton for mechanistic studies.⁵ This interest has promoted

development of some novel and useful syntheses of the ring system,⁶ but most of these are best adapted to the preparation of molecules substituted in a single ring. The preparation of bicyclo[3.3.1]nonanes with

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