Synthesis and Stereochemistry of Tricyclo[3.2.2.0^{2,4}]nonane Derivatives[1]

George R. Wenzinger* and José A. Ors

Department of Chemistry, University of South Florida, Tampa, Florida 33620

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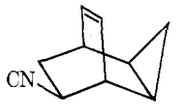
The four isomeric tricyclo[3.2.2.0^{2,4}]nonan-6-ols have been prepared along with two related tricyclo[3.2.2.0^{2,4}]-non-8-en-6-ols. The compounds with an exo cyclopropyl ring were prepared *via* the ketone, *exo*-tricyclo[3.2.2.0^{2,4}]-non-8-en-6-one, by $LiAlH_4$ reduction and hydrogenation. The endo cyclopropyl compounds were derived from *endo*-tricyclo[3.2.2.0^{2,4}]non-6-ene *via* standard methods. The stereochemistry of these alcohols has been elucidated with the aid of the nmr spectra of the Eu(fod)$_3$ complexes.

The chemistry of bridged polycyclic compounds containing a cyclopropane ring has provided considerable insight into the nature of the ability of this three-membered carbocycle to stabilize cationic species.[2] As an outgrowth of our previous work on the tricyclo[3.2.1.0^{2,4}]octyl system, synthetic work toward the closely related tricyclo-[3.2.2.0^{2,4}]nonyl skeleton was undertaken.

Two major problems exist: (1) the construction of the tricyclo[3.2.2.0^{2,4}] carbon skeleton, and (2) the elucidation of the stereochemistry of the four isomeric tricyclo-[3.2.2.0^{2,4}]nonan-6-ols.

Synthesis. The most common routes into this type of tricyclic system involve either cyclopropanation of bicyclic olefins or Diels–Alder and [2 + 2 + 2] cycloadditions. Our experience with the cyclopropanation of bicycloheptadiene[2a] led us to prefer the second general pathway. The scheme leading to the successful synthesis is given in Scheme I.

The tricyclic unsaturated ketone **2** was chosen as the point of entry into the compounds which we term the exo cyclopropyl series. This ketone was prepared from the acrylonitrile adduct of cycloheptatriene.[3] This [2 + 2 + 2] cycloaddition reaction reaction produces three major products in a 3:3:1 ratio. It was clear that the two most prevalent materials were the exo and endo isomers of 8-cyanotricyclo[3.2.2.0^{2,4}]non-6-ene (**13** and **14**). Recently,



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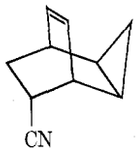

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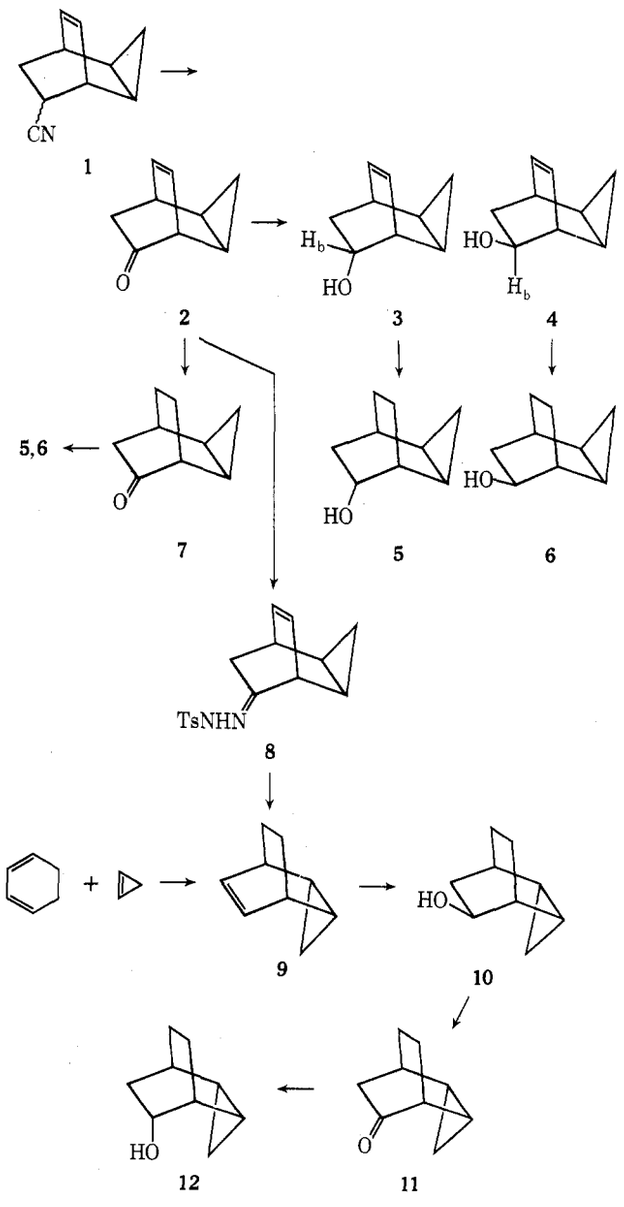
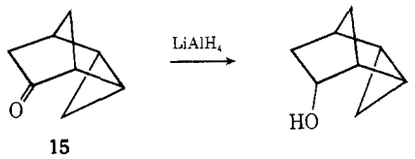
during the course of our work, Bellus, Helferich, and Weiss published a detailed study of this reaction bearing out our results as well as indicating the correct structure for the third product as 7-*endo*-cyanobicyclo[4.2.1]nona-2,4-diene.[4] This study also gave support for the exo or syn geometry for the cyclopropane ring in **2**. Their assignments based on nmr shifts agree well with our observations of the nmr spectra of related compounds. Furthermore, this stereochemistry is expected to predominate in this [2 + 2 + 2] cycloaddition, as is borne out by a number of examples.[3,4,5] Any doubt about this assignment being correct has been removed by consideration of the behavior of **2** and **7** upon reduction with $LiAlH_4$.

$LiAlH_4$ reduction of **7** is quite nonselective and yields a ~1:1 mixture of alcohols, *exo,endo*-tricyclo[3.2.2.0^{2,4}]nonan-6-ol (**5**) and *exo,exo*-tricyclo[3.2.2.0^{2,4}]nonan-6-ol (**6**).[6] This is consistent with the exo configuration for the cyclopropane ring, since models indicate that both faces of the carbonyl groups in **7** are quite similar; thus little reductive selectivity would be expected. From previous work[2a] on the reduction of ketone **15** we knew that an endo orientation of the cyclopropane ring, as in **11**, would lead to a large predominance of a single alcohol upon $LiAlH_4$ reduction. Whereas the nonselectivity in reduction of **7** served the purpose of indicating the exo orientation of the

Scheme I





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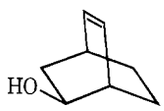
cyclopropane ring in 7 (and hence 2), it was not very useful for synthetic purposes. However, the $LiAlH_4$ reduction of 2 would be expected to be somewhat more selective based on the known reduction of bicyclo[2.2.2]oct-7-en-5-one, which produced a 3:1 mixture of exo and endo alcohols (16, 17).[7] It was quite gratifying to find that $LiAlH_4$



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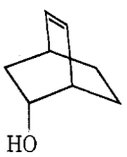

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reduction of 2 at −65° produced a 5:1 mixture of 4 and 3. The orientation of the alcohol groups follows from their modes of production and is borne out by the observation that the τ value for hydrogen H_b is slightly higher in 3 than in 4.[4] Furthermore, the vinyl hydrogens of 4 show a greater degree of nonequivalence in the nmr spectra than in 3 as expected if 4 contains an exo hydroxyl. Although these differences are convincing, the use of lanthanide shift reagents proved useful and decisively indicated that the initial assignment of geometry was correct (see the section on shift reagents). Hydrogenation of samples of 3 and 4 led to the desired exo series alcohols, 5 and 6.

The synthesis of the two endo cyclopropyl alcohols, 10 and 12, was quite direct. The Diels–Alder reaction between cyclopropene and cyclohexadiene[8] proceeded to yield the endo olefin 9 in approximately 10% yield. The structure of 9 is borne out by the 60-Hz nmr, which exhibited the following bands: 4.1 (2), 7.1 (2), 8.45 (4), 9.0 (2), 9.8 ppm (2). The endo configuration was expected on the basis of the analogous reaction of cyclopropene with cyclopentadiene[2a] and the previous synthesis by Rhodes.[8a] Convincing proof that this was indeed the correct stereochemistry for 9 came from direct conversion of 2 to 9 *via* the tosylhydrazone 8. Clearly, if 2 is as depicted above, then 9 must have the cyclopropane ring endo. Although this sequence served to correlate 2 and 9, in our hands it proved inadequate for the production of quantities of 9, for the yield was low and the product was difficult to purify. The endo orientation of the cyclopropane ring was further indicated in a striking fashion by the use of shift reagents on the alcohols 10 and 12. These could be prepared easily by hydroboration–oxidation of the tricyclic olefin 9 with diborane to yield >90% of a single alcohol (10). Further Sarett oxidation of 10 produced the endo ketone 11, which upon $LiAlH_4$ reduction produced 12 stereoselectively. The production of 12 upon $LiAlH_4$ reduction of 11 to the virtual exclusion of 10 again supports the endo configuration for the cyclopropane ring in 12.

Nmr Shift Reagents[9] and Stereochemistry. In order to supply additional evidence regarding the relative[9] stereochemistry of these compounds, alcohols 3, 4, 10, and 12 were studied using the lanthanide shift reagent $Eu(fod)_3$.[10] Alcohols 3 and 4 were chosen as representatives of the exo cyclopropyl series mainly because their nmr spectra were somewhat easier to interpret than those of 5 and 6 owing to the absence of the methylene groups which absorb in the τ 8–9 region.

Since initially only small quantities of the exo cyclopropyl series alcohols 3 and 4 were available, we chose to purify these compounds just prior to use by passing them through a glpc column and directly into carbon tetrachloride. This procedure was necessary owing to the tendency of 3 and 4 to form aerosols unless collected in a solvent. Secondly, this procedure excluded water, which has an adverse affect on the use of shift reagents.[11] For this reason the absolute concentration of the alcohols was known only within about ±10%. In all cases the concentration of the alcohol was similar but was not known absolutely. Observation with alcohols of the tricyclo[3.2.1.0^{2,4}]octyl skeleton of *known stereochemistry* indicated that this procedure using similar concentrations was adequate for gross stereochemical assignments so long as the lanthanide shifts to be compared were large as they are for the critical protons in 3, 4, 10, and 12. Since we worked in the region of low L/S ratios (L = lanthanide shift reagent, S = substrate) the shifts observed were essentially linear with L/S ratios.[9,12,13] This many times allows the estimation of an optimum L/S ratio for clear band separation without recourse to high L/S ratios where maximum shifts are observed. As is common in this type of work it is assumed that the stoichiometry of the LS complex[14] is the same for all alcohols. This would appear a safe assumption owing to the near equality of the two bridges in these molecules. The possible exception would be with compound 12, where it might be less probable to have LS_2 complexes owing to interference of the cyclopropyl methylene hydrogens with the $Eu(fod)_3$. If it were true that 12 formed LS_1 or predominantly LS_1 complexes rather than LS_2, then we should have observed smaller shifts for 12 at comparable L/S ratios for hydrogens b, c, and c′.[15] This was not observed. Furthermore, at low L/S ratios LS_2 complexes would be expected to predominate.[14]

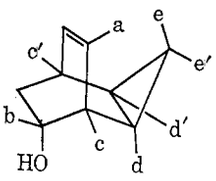
With the assumptions above, the shift data can be analyzed qualitatively. (For quantitative evaluation see ref 16)

Since all L/S ratios were probably within 10–15% of one another as shown by the relative constancy of the shifts for b, c, and c′ protons,[17] the observed shift of proton b will be used as essentially an internal standard. The shifts in hertz are taken as the shift in the center of gravity of a peak in the presence of $Eu(fod)_3$.

It is quite evident that the alcohol assigned the endo hydroxyl (3) exhibits an extraordinarily large shift for the d and d′ cyclopropyl hydrogens (118 Hz), whereas the exo alcohol 4 shows a much smaller shift (26 Hz). Furthermore, the signals for these hydrogens clearly separate from one another in the endo alcohol 3 but remain together in 4. It must be emphasized that since the concentrations of the alcohol relative to the europium compound are not exactly the same, the absolute values of the shifts are not extremely meaningful. The relative values are important, particularly when compared to the shift of H_b in the two alcohols, 135 Hz for 4 *vs.* 181 Hz for 3. Since at equal L/S ratios these values would have been nearly equal,[18] it is apparent that the shifts expected for d and d′ in compound 3 would still be large, around 90 and 44 Hz, respectively, at concentrations equal to 4. These large shifts are accompanied by less spectacular shifts for other groups of protons, as seen in Table I. Note that the olefin hydrogens, a, of 4 are shifted by a larger amount than those for 3. It is also of interest to note that the olefin pattern of 4 becomes much more similar to that for 3 after addition of europium reagent. The exact origin of this effect is not clear; however, the greater shift for the a proton in 4 relative to 3 support the assigned structures. Note also that the e and e′ hydrogens are shifted by a small amount in both 3 and 4. This is to be contrasted sharply with the data for 10 and 12 presented in Table II.

Owing to greater overlapping of bands with these two alcohols (10, 12) it is more difficult to assign the bands when using $Eu(fod)_3$. However, it is quite clear that H_e and $H_{e'}$, which overlap in both the endo,exo (10) and the endo,endo compound (12), behave in a strikingly different manner in the two compounds in the presence of the europium reagent. For the alcohol 10 these bands remain together and shift about 26 Hz, whereas for the alcohol 12

Table I
Eu(fod)$_3$ Shift Study for Alcohols 3 and 4



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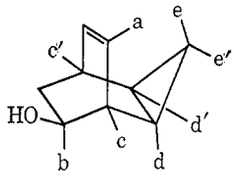

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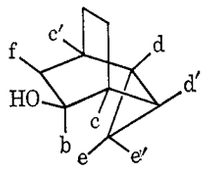
H	ΔHz	H	ΔHz
H_b	−181	H_b	−135
H_a	−31	H_a	−50
H_c	−101	H_c	−92
$H_{c'}$	−34	$H_{c'}$	−30
H_d	−118	H_d	−26 unresolved
$H_{d'}$	−55	$H_{d'}$	−26
$H_{e,e'}$	(−34) unresolved	$H_{e,e'}$	(−18) unresolved

Table II
Eu(fod)$_3$ Shift Study for Alcohols 10 and 11[a]



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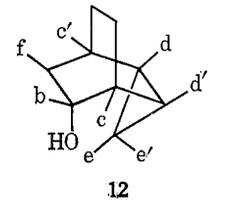

12

H	ΔHz	H	ΔHz
H_b	−177	H_b	−176
H_c	−124	H_c	−129
$H_{c'}$	−30	$H_{c'}$	−48
$H_{d,d'}$	−32	$H_{d,d'}$	−53
H_e	−29	H_e	−181 (133)[b]
$H_{e'}$	−29	$H_{e'}$	−56
H_f	−161	H_f	−67

[a] The relative concentration of alcohol to Eu(fod)$_3$ would appear to be quite similar for these two alcohols, as can be seen from the similar values for the shift for both H_b and H_c. This does assume a similar position for the Eu atom relative to protons H_b and H_c, which is certainly very reasonable for H_b (see ref 14 for similar case) and not surprising for H_c. [b] Since there is some overlap of bands, it is difficult to be totally certain of the assignment of this band. The 181 value appears more consistent with the values of H_c and $H_{c'}$ considering reasonable positions for the Eu atom and estimated distances from models.

(endo OH) they clearly separate. In fact it appears that H_e in **12** exhibits the greatest shift (181 Hz) of any hydrogen in these molecules. Even if the value of 133 Hz is used rather than 181 Hz, assuming an alternate assignment, it is obvious that H_e in **12** must be quite proximate to the europium atom, as could only be possible for the endo,endo alcohol. Furthermore, the considerably smaller spread in shifts for H_d and $H_{d'}$ in these two compounds relative to **3** and **4** again clearly indicates that the geometries of **10** and **12** are as depicted. Thus even in the absence of accurate knowledge of relative concentrations of reagents it appears that Eu(fod)$_3$ is quite useful not only in resolving overlapping bands but also in supplying confirmation of the assumed gross geometry of rigid systems of this type.

The synthesis and stereochemistry of these compounds complete the first phase of this work. Data regarding solvolysis behavior will be presented elsewhere.

Experimental Section

All melting points are uncorrected. Nmr spectra were recorded on a Varian A-60A spectrometer with internal standard TMS in CCl_4. Chemical shifts are reported in τ values with the number of protons in parentheses. The europium shift reagent [Eu(fod)$_3$] was supplied by Norell. Infrared spectra were obtained on a Perkin-Elmer Model 137 grating spectrophotometer. Microanalysis were by Galbraith Laboratories, Knoxville, Tenn. The following glpc columns were employed: FFAP (15%) 10 ft × 0.375 in. (A); FFAP (10%) 30 ft × 0.375 in. (B); XF-1150 (20%) 5 ft × 0.25 in. (C); Carbowax 20 M (15%) 10 ft × 0.375 in. (G); Dow 710 5 ft × 0.25 in. (F).

Tricyclo[3.2.2.0^{2,4}]non-8-en-6-one (2). The procedure of Freeman[3] was followed and the purity was ascertained by glpc on columns B, C, and G. Nmr data agrees with those reported in ref 3.

exo-**Tricyclo[3.2.2.0^{2,4}]nonan-6-one (7).** To a prehydrogenated suspension of 0.1 g of 5% palladium on carbon was added a solution of 2.42 g of **2** in 35 ml of dry ether. Hydrogenation was allowed to proceed until no further hydrogen was absorbed. Filtration and ether washing of the catalyst led upon evaporation of the ether to the product which was distilled at 80° (1 Torr) to yield 1.87 g (76%) of pure **7**: mp 113–114°; glpc (B) indicated one compound; nmr τ 7.59–7.95 (4) m, 8.5 (4) m, 8.7–9.6 (4) broad m; ir 3010, 2950, 1730, 1745 cm^{-1}.

Anal. Calcd for $C_9H_{12}O$: C, 79.41; H, 8.82. Found: C, 79.52; H, 8.89.

exo,exo-**Tricyclo[3.2.2.0^{2,4}]nonan-6-ol and** *exo,endo*-**Tricyclo[3.2.2.0^{2,4}]nonan-6-ol. A. Reduction of 7 with LiAlH$_4$.** A mixture of 1.9 g of $LiAlH_4$ in 250 ml of anhydrous ether was added, dropwise, to a solution of 6.7 g of **7** in 35 ml of diethyl ether. The resulting suspension was stirred for 27 hr at room temperature and then treated with excess saturated sodium sulfate solution. Filtration followed by the removal of the solvent gave a soft solid, which was subjected to glpc on column B. Two products were present in a 1:1 mixture. These could be separated with difficulty by glpc; hence these two alcohols are better prepared by method B.

B. Reduction of 2 with LiAlH$_4$. *exo*- **and** *endo,exo*-**Tricyclo[3.2.2.0^{2,4}]non-8-en-6-ol.** To a solution of $LiAlH_4$ in ether at −65° was added dropwise a solution of 1.9 g of **2** in 35 ml of ether. After stirring for 24 hr at −65° the solution was allowed to warm and was worked up as in A to yield a quantitative yield of crude product. Preparative glpc separation (B) lead to **4** and **3** in the ratio of 5:1 with melting points of 87–90 and 104–107°, respectively: nmr (**4**) τ 4.25 (2) m, 6.15 (1) 2 t, 7.17 (3) m, 8.0 (1) m, 8.79 (1) t, 9.22 (2) m, 9.85 (2) m; nmr (**3**) τ 4.2 (2) t, 6.18 (1) 5, 7.2 (2) m, 8.21 (1) m, 8.7 (1) m, 8.85 (2) m, 9.9 (2) m.

Anal. Calcd for $C_9H_{12}O$ (**4**): C, 79.41; H, 8.82. Found: C, 79.25; H, 8.70.

Anal. Calcd for $C_9H_{12}O$ (**3**): C, 79.41; H, 8.82. Found: C, 79.54; H, 8.58.

Hydrogenation of 3 and 4. Hydrogenation of ethanol solutions of pure **3** and **4** over 5% Pd/C was carried out at atmospheric pressure until the uptake of 1 mol of hydrogen was complete. Filtration and removal of the solvent led to quantitative yields of **5** and **6**. Glpc (B) data indicated a single compound in each instance. The melting points of glpc (pure) samples follow: **6**, 155–185.5° (softens at 150°); **5**, 144–147° (softens at 130°).

Anal. Calcd for $C_9H_{14}O$ (**5**): C, 78.26; H, 10.14. Found: C, 78.65; H, 9.99.

Anal. Calcd for $C_9H_{14}O$ (**6**): C, 78.26; H, 10.14. Found: C, 78.23; H, 10.19.

endo-**Tricyclo[3.2.2.0^{2,4}]non-6-ene (9). A. Diels–Alder Reaction.** A slow stream of cyclopropene in nitrogen, generated from 23 g of allyl chloride and 12 g of $NaNH_2$ at 85–105° according to the procedure of Closs,[19] was passed into a stirred solution of 11.0 g (0.136 mol) of 1,3-cyclohexadiene in 150 ml of dry methylene chloride at room temperature. After the production of cyclopropene was complete (5 hr) the system was flushed with N_2 for another 2 hr. The methylene chloride solution was then washed successively with cold 10% hydrochloric acid, 10% sodium carbonate, and water and then dried over magnesium sulfate. Removal of the solvent at atmospheric pressure followed by distillation up to 79° led to recovered diene. Distillation at 20 Torr at 120–130° led to 3.1 g (11% based on allyl chloride) of **9**, which crystallized and exhibited a melting point of 54°. Glpc (A) indicated a single compound, nmr τ 3.05 (2) t, 7.1 (2) m, 8.4 (4) m, 9.0 (2) m, 9.85 (2) t.

B. Reduction of Tosylhydrazone 8. To a stirred solution of 2.7 g (0.01 mol) of tosylhydrazone **8** in 75 ml of tetrahydrofuran was added 5.0 g (0.13 mol) of $LiAlH_4$. This mixture was refluxed for 40 hr followed by cooling and work-up with saturated sodium sulfate solution. The organic layer was washed with dilute acid and 10% Na_2CO_3 solution followed by water and then dried with magnesium sulfate. Removal of the solvent led to recovery of unreacted **8**, which was separated by filtration. The residual oil was shown by glpc (A and F) to consist of two products in the ratio of 4:1. The major component, present in 57% overall yield, was **9** as

shown by nmr and ir spectra. Purification of this product other than by glpc proved difficult.

endo,exo-**Tricyclo[3.2.2.0^{2,4}]nonan-6-ol (10).** A solution of 7.2 g of olefin **9** in 100 ml of tetrahydrofuran at 0° was treated with a stream of diborane generated from a solution of 4.75 g of $NaBH_4$ in diglyme and 25 ml of $BF_3 \cdot Et_2O$ in 30 ml of diglyme according to the procedure previously used.[2a] This led to 7.31 g (87%) of a solid which upon crystallization from pentane had mp 165–168°. Glpc (B) of the original mixture indicated greater than 90% of a single alcohol, **10**, nmr τ 6.4 (1) m, 6.95 (1) 5, 8.15 (3) m, 8.5 (3) m, 8.88 (1) m, 8.18 (2) m, 9.8 (2) m.

Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 77.98; H, 10.05.

endo-**Tricyclo[3.2.2.0^{2,4}]nonan-6-one (11).** To a stirred suspension of 25 g of chromic acid in 250 ml of pyridine at 0° was slowly added a solution of 7.3 g of alcohol **10** in 80 ml of pyridine. The mixture was stirred for 39 hr at room temperature followed by addition of 100 ml of water and extration ten times with 150-ml portions of pentane. The pentane extracts were washed with cold 10% hydrochloric acid, 10% sodium carbonate, and water. After drying and removal of the solvent through a Vigreux column, 5.86 g of crude ketone **11** was obtained. Glpc (B) indicated only 65% purity. Distillation at 100° (0.5 Torr) yielded the pure ketone: $n^{24}D$ 1.5094; nmr τ 7.55 (2) m, 8.15 (2) d, 8.31 (4) m, 8.91 (2) m, 9.72 (2) m.

Anal. Calcd for $C_9H_{12}O$: C, 79.41; H, 8.82. Found: C, 79.52; H, 8.99.

endo,endo-**Tricyclo[3.2.2.0^{2,4}]nonan-6-ol (12).** To a solution of lithium aluminum tri-*tert*-butoxyhydride at −65°, prepared according to the procedure of Brown,[20] was added 0.9 g (0.007 mol) of ketone **11** in 15 ml of tetrahydrofuran. After 24 hr at this temperature the reaction mixture was warmed to room temperature and worked up as in the other reductions. Glpc analysis indicated 79% of a single alcohol, mp 136–140°, nmr τ 6.3 (1) m, 7.08 (1) s, 8.0 (2) m, 8.5 (5) m, 8.9 (1) t, 9.2 (2) m, 9.7 (2) m.

Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.42; H, 10.31.

Europium Shift Reagent Studies. The $Eu(fod)_3$ used was taken directly from a fresh bottle supplied by Norell. The alcohols were subjected to glpc purification directly before use and then dissolved in CCl_4 for analysis. The shift reagent was weighed out and added in increments of about 10 mg, after which the nmr was observed and recorded. Since in many instances the peaks were broad, the centers of gravity of the peaks were used and shift values were deduced from these.

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Registry No.—**2**, 50744-35-9; **3**, 50744-41-7; **4**, 50898-31-2; **5**, 51260-36-7; **6**, 51260-35-6; **7**, 51260-37-8; **8**, 50744-36-0; **9**, 27019-95-0; **10**, 51260-33-4; **11**, 51260-38-9; **12**, 51260-34-5; cyclopropene, 2781-85-3; 1,3-cyclohexadiene, 592-57-4.

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Synthesis and Relative Stereochemical Assignment of the Four Isomeric Cyclopropane-Bridged Tricyclo[3.2.2.0^{2,4}]nonan-6-ols[1,2d]

Paul E. Schueler[2a,b] and Yorke E. Rhodes*[2c]

Department of Chemistry, New York University, New York, New York 10003

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The four isomeric tricyclo[3.2.2.0^{2,4}]nonan-6-ols, containing a cyclopropane ring fused in a homocyclopropylcarbinyl relationship to the alcohol functionality, have been synthesized from the corresponding alkenes. Stereochemical assignments are accomplished by chemical means and with the aid of nmr shift reagents.

Reactivity studies[3] of various policyclic compounds containing bridged or fused cyclopropane rings have revealed the great diversity of reactivity of 2-cyclopropylethyl derivatives from the highly activated and reactive[3a,b,e-h] to the highly deactivated and unreactive[3c,d] systems. Despite the inherent problems of dissecting strain effects from electronic interaction effects and neighboring group effects, we have extended our earlier work[4] with conformationally unrestrained 2-cyclopropylethyl systems to studies using compounds with structural frameworks that have geometries and relative orientations of reactive groups that are well defined, namely, the four isomeric tricyclo[3.2.2.0^{2,4}]nonan-6-ols (*endo,endo-*, *endo,exo-*, *exo,endo-*, and *exo,exo-*)[5] in which there are four correspondingly different homocyclopropylcarbinyl geometrical orientations. Solvolyses of the parent 2-bicyclo[2.2.2]octyl system are not strongly assisted by neighboring carbon participation and thus any resultant cyclopropane participation should appear in rate and product studies of the solvolyses and should not be swamped[6a] by the dominant