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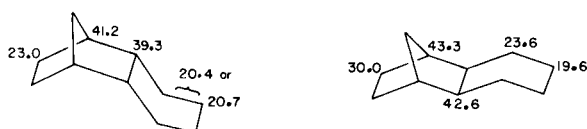
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The stereoselective synthesis of *cis*-fused 1,4-epoxydecahydronaphthalenes from transannular reactions of medium-ring compounds is described. The carbon-13 nmr spectra of both are reported, and assignments of the various resonances have been made based on model compounds and off-resonance decoupling experiments.

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The ^{13}C nmr spectra of *endo*- and *exo*-tetramethylenenorborane (Figure 1) were recently reported (1), and interesting correlations between chemical shifts and configurations were made. We felt it would be instructive to compare their ^{13}C nmr spectra with those of the

Figure 1



heterocyclic analogs, 1,4-epoxydecahydronaphthalenes **3** and **6** (see Scheme 1). Also, some confusion exists in the literature concerning these two compounds (2), and therefore the full characterization of both isomers appeared to be profitable to clear up this discrepancy. The compounds were synthesized by cyclizations involving

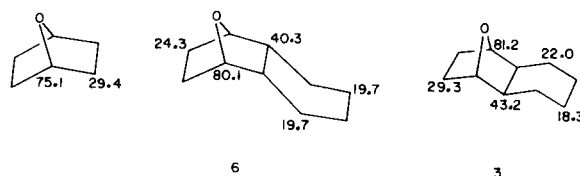
cis,trans-1,5-cyclodecadiene and its monoepoxide, chosen for their propensity for highly regio- and stereospecific reactions (3-8).

The first attempt to prepare these compounds was to cyclize *cis,trans*-1,5-cyclodecadiene to *cis,cis*-1-decahydronaphthol **1**, by a one-step method (Scheme 1) similar to Tranyham's two step method (9). This compound was then expected to cyclize to 1,4-epoxydecahydronaphthalene by Cope's method (4,11) of treating a medium-ring alcohol with lead tetraacetate. However, no reaction was observed even after 49 hours reflux in dry benzene.

However, the bromohydrin **2** was prepared in high yield by adding bromine to *cis,trans*-1,5-cyclodecadiene in wet DMSO. A similar method was concurrently demonstrated by other workers (7). Stirring **2** in ethanol/potassium hydroxide gave **3** in a much higher yield than the method reported earlier (2). The diol **5** (5) can also be cyclized to **3** upon heating over alumina (2,12), but the yield is very low.

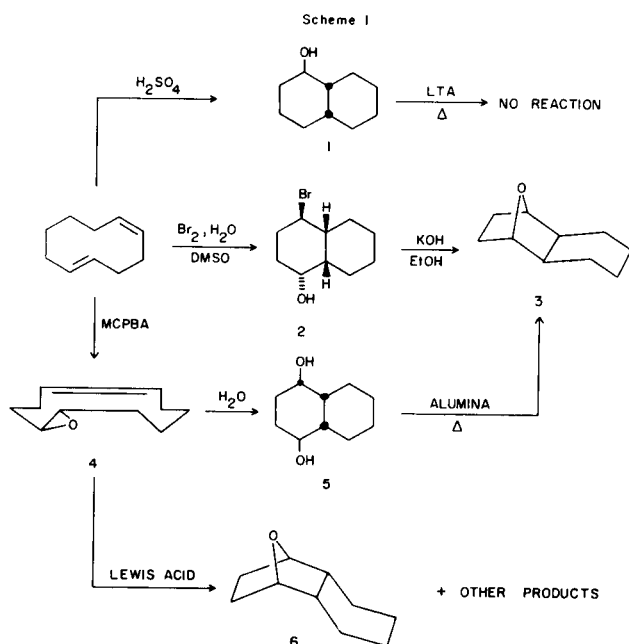
Earlier, we prepared **6** (8) by treating the monoepoxide **4** with diethylmagnesium (2 octalols, easily separable from **6**, were also formed). Repeated attempts to improve this synthesis by using other Lewis-acids were unsuccessful. Treatment of **4** with boron trifluoride in ether did not give any detectable **6** (8), whereas the weaker Lewis acid stannic chloride did yield some, albeit neither reagent afforded a synthetically useful procedure (13). Diethylzinc behaved like diethylmagnesium (8), and gave **6** in approximately 25% yield

Figure 2



6

3



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The assignment of resonances for **3** and **6** (Figure 2) is based on the model hydrocarbon analogs (*vide supra*) and on 7-oxabicyclo[2.2.1]heptane (Figure 2), along with off-resonance decoupling experiments. Peaks at 80.1 and 81.2, both doublets in off-resonance decoupled spectra, were easily assigned to the oxygen bridgehead carbons for **6** and **3**, respectively. The other doublets in these compounds were therefore assigned to the carbon-carbon bridgehead positions. The remaining assignments are based on the hydrocarbon analogs.

The degeneracy of peaks for **6** at 19.7 is fairly remarkable for such a simple molecule (14-16), but *endo*-tetramethylenenorborane almost has a degeneracy since peaks occur at 20.4 and 20.7 ppm. In the *endo*-isomer some steric compression (14) causes upfield shifts at the terminal carbons (24.3 ppm *versus* 29.3 ppm for the *exo*-isomer), and this appears to be somewhat general (14,17). Substituents on this type of position have been shown to suffer upfield shifts from the same configurational effects (17). This steric compression suggests the contribution of a configuration with β -axial type carbons close to the carbons giving resonance at 24.3.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Infrared spectra were obtained in a Perkin-Elmer Infracord spectrophotometer. Gas chromatographic analyses were performed on a Wilkens Aerograph A-90-P with 10 ft. x 0.25 in. columns packed with 3% SE-30 or 10% FFAP on Chromosorb W. Pmr analyses were done on a Varian A-60 NMR spectrometer, and cmr on a Bruker WH-90 FT NMR spectrometer at 22.63 MHz using deuteriochloroform solvent with TMS as an internal standard. A JMS-07 GC/MS was used to record mass spectral data.

Synthesis of *cis,cis*-1-Decahydronaphthol (**1**).

A 1.36 g. (0.01 mole) sample of *cis,trans*-1,5-cyclodecadiene was combined with 0.9 ml. of concentrated hydrochloric acid (0.009 moles), 12 ml. of water and 24 ml. of dioxane. The mixture was refluxed with stirring for 4 hours, and then the water and dioxane were removed under vacuum, leaving *cis,cis*-1-decahydroaphthol (**1**). Recrystallization from petroleum ether gave 0.55 g. of pure, isolated **1**, m.p. 89-91° (lit. (9) m.p. 89-91°). Nmr and ir spectra were identical to those of an authentic sample (9). Stirring 2.36 g. of cyclodecadiene in 0.5 ml. of sulfuric acid, 12 ml. of water and 24 ml. of dioxane for 10 hours at ambient temperature gave 40-50% yields.

Synthesis of *trans*-4-Bromo-*cis,cis*-1-decahydronaphthol (**2**).

To an ice cooled solution of 1.0 g. of water, 20 ml. of DMSO, 5 ml. of carbon tetrachloride and 3.04 g. of *cis,trans*-1,5-cyclodecadiene (0.22 mole), was added 3.2 g. of bromine (0.02 mole) in 10 ml. of carbon tetrachloride. The mixture was stirred 0.5 hour, and then extracted with ether. The ether layer was washed with saturated bicarbonate, water, and dried (sodium sulfate). After concentrating the sample, the oil was triturated with pentane or left to crystallize in a freezer for two days. Titration gave 2.8 g. of **2** (60% yield), m.p. 122-124° (lit. (7) m.p. 124-125°). The nmr and ir spectra were identical to that of an authentic sample prepared by another route (6).

exo-1,4-Epoxydecahydronaphthalene (**3**).

A mixture of 0.23 g. of **2** (1 mmole), 0.60 g. of fused potassium hydroxide and 25 ml. of anhydrous ethanol was refluxed for 21 hours. The mixture was then neutralized with 7% hydrochloric acid, and the mixture was continually extracted overnight with ether. After drying, 0.15 g. of liquid was obtained, 85-90% of which was **3** (85% yield) [b.p. 91-93° (20 mm), n_D^{25} 1.4885 (lit. (2) 1.4889-1.4988)]; nmr (carbon tetrachloride): δ 4.0 (multiplet, 2H) and 1.0-1.9 (multiplet, 14H); ms: M^+ (calcd.) 152.1200 for $C_{10}H_{16}O$, found 152.1255, 93 (78), 81 (81), 79 (85), 67 (85), 55 (81), 41 (87), 39 (83), 29 (100).

Compound **3** was also prepared by heating **4** in water (5) to give **5**. The diol was then heated to 200-250° over activated alumina (MCB AX 612-9296) according to the earlier method (2) and **3** distilled off in approximately 5% yield. The nmr and ir of the product were the same as above, proving that Wittbecker, Hall and Campbell's method gives **3**.

Details of the synthesis of **6**, *endo*-1,4-epoxydecahydronaphthalene, are given in reference 8.

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- (12) The diol, prepared by different route, was cyclized to a 1,4-epoxydecahydronaphthalene in the original synthesis mentioned in reference 2. This conclusively establishes the identity of the 1,4-epoxydecahydronaphthalene they prepared as **3**.
- (13) Complex product mixtures resulted and several compounds formed were unstable to glc or distillation.
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