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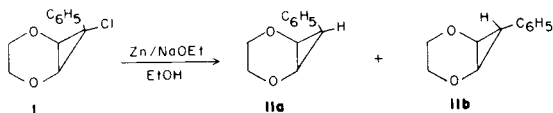
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The synthesis and stereochemical assignment of *exo*-7-phenyl-2,5-dioxabicyclo[4.1.0]heptane is reported. The stereochemical assignment was made based on data obtained from variable temperature nmr spectra.

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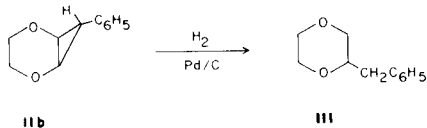
We have recently reported on making stereochemical assignments for the 7-phenyl-2-oxabicyclo[4.1.0]heptanes (1) and the 7-phenyl-3-oxabicyclo[4.1.0]heptanes (2) based on nmr considerations. We now wish to extend this study to include the synthesis and stereochemical assignment of *exo*-7-phenyl-2,5-dioxabicyclo[4.1.0]heptane.

Synthesis of the title compound was accomplished by the reduction of *exo*-7-chloro-*endo*-7-phenyl-2,5-dioxabicyclo[4.1.0]heptane, I (3), with activated zinc dust (4) in a 5% solution of sodium ethoxide (5). Gas chromatographic



analysis of the mixture revealed two volatile compounds in a 1:5.6 ratio, which were labeled in order of increasing elution times as IIa (6) and IIb. The major product of the reaction, IIb, was obtained in pure form by trapping on a gas chromatograph. Its gross structure was established by a correct elemental analysis for $C_{11}H_{12}O_2$, a molecular ion in its mass spectrum at m/e 176, and nmr absorptions at δ 6.7-7.4 (5H, multiplet), 3.5 (6H, singlet) and 2.2-2.4 (1H, triplet, $J = 3.3$). These data are in agreement with the assigned structure for IIb.

Additional evidence supporting the gross structure of IIb was obtained from its hydrogenation. Although the ir spectrum revealed no olefinic linkage, IIb absorbed one



equivalent of hydrogen upon catalytic hydrogenation, which is consistent with a cyclopropane moiety. The hydrogenation product, 2-benzyl-1,4-dioxane, III, was identified on the basis of a correct elemental analysis for $C_{11}H_{14}O_2$, and an nmr spectrum consistent with the assigned structure.

The stereochemical assignment of IIb was made based

strictly on nmr considerations. A coalescence of the phenyl absorption in the nmr spectrum of IIb was observed as the temperature was increased from 25° to 180° and the barrier for rotation of the ring overcome. This rotation is possible only with the *exo* isomer. This data is in agreement with the changes in the phenyl absorption observed as a function of temperature in the nmr spectra of the 7-phenyl-2-oxabicyclo[4.1.0]heptanes (1) and the 7-phenyl-3-oxabicyclo[4.1.0]heptanes (2).

EXPERIMENTAL

An F & M gas chromatograph, Model 810, was employed for all gas chromatographic analyses. Infrared spectra were obtained using a Beckman Model 10 grating infrared spectrophotometer with potassium bromide cells. Nmr spectra were recorded in carbon tetrachloride with a Varian A-60 spectrometer employing tetramethyl silane as an internal reference. Ultraviolet spectra were recorded with a Bausch and Lomb Model 505 spectrophotometer. The elemental analyses were performed by M-H-W Laboratories, Garden City, Michigan. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are corrected. Boiling points are uncorrected.

exo-7-Chloro-*endo*-7-phenyl-2,5-dioxabicyclo[4.1.0]heptane (I).

In a 3-necked 2 l flask equipped with a mechanical stirrer, calcium chloride drying tube and thermometer, benzal chloride (59.71 g, 0.3708 mole) was added dropwise for a period of 30 minutes into a solution of 166 g of potassium *t*-butoxide (7) in 800 ml of dry dioxene (8). After allowing the reaction to proceed at 75° for 6 hours, the mixture was cooled, washed with water, a saturated sodium chloride solution and then dried over magnesium sulfate. The mixture was then filtered, the solvent evaporated, and the residue distilled *in vacuo* to yield 25.2 g (32% yield) of I, bp 135-140°/1 mm, which solidified. Upon recrystallization from absolute ethanol, I had a mp of 74-75°; uv (cyclohexane): λ max 216 nm (ϵ 9850); molecular ions in the mass spectrum at m/e 210 and 212 (3:1 ratio); nmr (carbon tetrachloride): δ 7.2-7.8 (5H, multiplet), 3.9 (2H, singlet) and 2.8-3.6 (4H, multiplet).

Anal. Calcd. for $C_{11}H_{11}ClO_2$: C, 62.71; H, 5.26; Cl, 16.83; O, 15.19. Found: C, 62.63; H, 5.34; Cl, 17.03; O, 15.00.

exo-7-Phenyl-2,5-dioxabicyclo[4.1.0]heptane (IIb).

To a vigorously stirred solution of sodium ethoxide (5) prepared from 405 ml of absolute ethanol and 16.2 g of sodium were added 13.5 g of activated zinc dust (4) and 9.0 g (0.0428 mole) of I. The mixture was refluxed for 40 hours, cooled, decanted and filtered. The filtrate was taken up in ether, washed with water, a saturated sodium chloride solution and dried over magnesium sulfate. The ether was evaporated and the residue

distilled *in vacuo* to yield 5.18 g (69%) of a mixture of IIa and IIb, bp 96-97°/1 mm. Pure IIb was then obtained by trapping on the gas chromatograph; molecular ion in the mass spectrum at *m/e* 176; nmr (carbon tetrachloride): δ 6.7-7.4 (5H, multiplet), 3.5 (6H, singlet) and 2.2-2.4 (1H, triplet; $J = 3.3$).

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86; O, 18.16. Found: C, 74.92; H, 6.97; O, 18.29.

Hydrogenation of *exo*-7-Phenyl-2,5-dioxabicyclo[4.1.0]heptane (IIb).

Hydrogenation of 1.0 g (0.0057 mole) of IIb was carried out in 50 ml of absolute ethanol and 0.1 g of 5% Palladium on charcoal in a Parr reaction apparatus (50 psi) for 48 hours. The solution was filtered, the alcohol evaporated and the residue distilled *in vacuo* to give 0.92 g (91%) of III, bp 107°/2 mm; nmr (carbon tetrachloride): δ 7.2 (5H, singlet) and 2.4-3.8 (9H, multiplet).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; O, 17.95. Found: C, 74.08, H, 7.96; O, 17.96.

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