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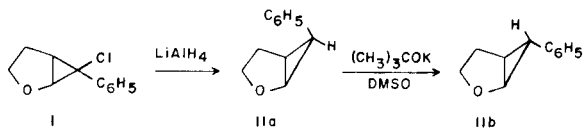
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Preparation and stereochemical assignments of the 6-phenyl-2-oxabicyclo[3.1.0]hexanes are reported. The stereochemical assignments are based on chemical as well as nmr data.

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Recently, we have reported the stereochemical assignments of several $(n + 3)$ -bicyclo $[n.1.0]$ alkanes based on variable temperature nmr data [1,2]. These compounds can be prepared by reducing the adducts obtained from the reaction of benzal chloride, potassium *t*-butoxide and the appropriate olefin. As part of our continuing study, we now wish to report the synthesis and stereochemical assignments of the 6-phenyl-2-oxabicyclo[3.1.0]hexanes.

The *endo*- and *exo*-6-chloro-6-phenyl-2-oxabicyclo[3.1.0]hexanes, I, were prepared by reacting benzal chloride, potassium *t*-butoxide and 2,3-dihydrofuran. The structure assigned to I was supported by its nmr spectrum which furnished absorptions at δ 7.2-7.6 (m, 5H), 4.2-4.3 (m, 1H), 3.5-3.9 (m, 1H), and 1.6-2.8 (m, 4H), an ultraviolet absorption band at 216 nm (ϵ 8480), which has been shown to be characteristic of the phenyl substituted cyclopropanes [1-4], and a correct elemental analysis for $C_{11}H_{11}ClO$.



The reduction of I with lithium aluminum hydride [5,6] produced *endo*-6-phenyl-2-oxabicyclo[3.1.0]hexane, IIa. The structure of IIa was established by its nmr spectrum which showed absorptions at δ 6.9-7.4 (m, 5H), 4.0-4.3 (m, 1H), 3.5-3.8 (m, 1H), 2.3-2.6 (m, 1H), and 1.5-2.1 (m, 4H), an ultraviolet absorption band at 211.5 nm (ϵ 10,100) with a shoulder at 218.2 nm (ϵ 8420), and a correct elemental analysis for $C_{11}H_{12}O$.

The base equilibration of IIa with a 10% solution of potassium *t*-butoxide in dry dimethyl sulfoxide [7] produced *exo*-6-phenyl-2-oxabicyclo[3.1.0]hexane, IIb. The structure of IIb was established in the same manner as IIa.

Further evidence of the gross structure of IIa and IIb was obtained by hydrogenation of these compounds. The ir spectra of IIa and IIb showed no absorptions due to isolated double bonds, yet upon catalytic hydrogenation, each absorbed one equivalent of hydrogen. This behavior is characteristic of cyclopropyl rings. Hydrogenation of IIa produced two compounds, III and IV (numbered in order of elution) in a ratio of 6.22:1, respectively, while IIb pro-

duced the same two compounds in a ratio of 1:2.27. Compound III was identified as 2-benzyltetrahydrofuran and IV was identified as 3-benzyltetrahydrofuran based on their nmr spectra and correct analytical analyses. These compounds are the expected products of the hydrogenation of IIa and IIb [1,2].

The stereochemical assignments of IIa and IIb were made based on chemical as well as spectral data. Chemical evidence supporting these assignments, was obtained from the base equilibration of IIa producing the more thermodynamically stable *exo* form IIb [7]. This equilibration is possible only if IIa is the *endo* isomer. Further evidence supporting these assignments was obtained from the reduction of I with lithium aluminum hydride to form IIa. This reaction has been shown to be stereoselective producing the *endo* isomer when reacted with bicyclic compounds analogous to I [5,6].

Spectral evidence supporting these assignments is obtained from variable temperature nmr data [1,2]. The spectra of IIa at 170° showed no significant differences in the phenyl absorption patterns when compared to its spectra at 34° however, the same was not true for IIb. Compound IIb showed much more spin-spin splitting at low temperatures than at higher temperatures. Inspection of models of these compounds demonstrates that the phenyl ring is much freer to rotate in IIb than in IIa. Thus, the ortho protons become more magnetically equivalent resulting in less spin-spin splitting.

EXPERIMENTAL

The nmr spectra were recorded in deuteriochloroform and hexachlorocyclopentadiene with a Varian EM-390 spectrometer employing tetramethylsilane as an internal reference. Infrared spectra were obtained using a Nicolet ir spectrometer, Model MX-1. A Hewlett Packard gas chromatograph, Model 5840A, equipped with a thermal conductivity detector, was employed for all gas chromatographic analyses. An 8' \times 1/8" copper column packed with 10% Ucon 50 HB 2000 (polar) oil on Chromosorb P operated at 110° was employed for routine analysis. An 8' \times 1/4" copper column packed with 10% Ucon 50 HB 2000 (polar) on Chromosorb P operated at 160° was employed for trapping IIa, IIb, III and IV. Ultraviolet spectra were recorded in cyclohexane with a Beckman Model DK-2A spectrophotometer. The elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Boiling points are uncorrected.

6-Chloro-6-phenyl-2-oxabicyclo[3.1.0]hexane (I).

In a 2000 ml three-necked flask equipped with a mechanical stirrer, a reflux condenser, a dropping funnel, and a thermometer, a solution of 500 g of 2,3-dihydrofuran and 185 g of potassium *t*-butoxide was heated to 55°. Then 88.6 g of benzal chloride was added over a period of 1.5 hours and allowed to reflux for 3 hours [4]. The solution was cooled to room temperature and an equal volume of water added. The solution was placed in a separatory funnel, the organic layer extracted with ether, washed with water until the aqueous layer was neutral, and dried over calcium chloride. The ether was then evaporated *in vacuo* and the residue distilled yielding 40.1 g (37% yield, 90% pure by vpc) of I. Purification of I [4] was accomplished by passing a stream of 3% ozone through a wash bottle containing 100 ml of 95% acetic acid, 12.5 g of I, and a magnetic stirrer. The gas was then passed through a 2% potassium iodide trap and the reaction allowed to proceed for 5 minutes after the appearance of iodine in the trap. Then 45 ml of a 10% solution of hydrogen peroxide was added and allowed to stir overnight. The organic layer was extracted with ether, washed with base, washed with water, and dried over calcium chloride. The ether was evaporated *in vacuo* and the residue distilled yielding 10.35 g (83% yield, 99% pure by vpc) of I, bp 95-97/1 mm; nmr (deuteriochloroform): δ 7.2-7.6 (m, 5H), 4.2-4.3 (m, 1H), 3.5-3.9 (m, 1H), and 1.6-2.8 (m, 4H); uv (cyclohexane): λ max 216 nm (ϵ 8480).

Anal. Calcd. for C₁₁H₁₁ClO: C, 67.87; H, 5.70; Cl, 18.21; O, 8.22. Found: C, 68.07; H, 5.92; Cl, 17.99; O, 8.41.

endo-6-Phenyl-2-oxabicyclo[3.1.0]hexane (IIa).

To 20 ml of dry diglyme in a 100 ml four-necked flask equipped with a magnetic stirrer, thermometer, calcium chloride drying tube, and a dropping funnel, one gram of lithium aluminum hydride was added and the solution cooled to 25°. To this solution was added one gram of I mixed with twice its volume of diglyme [5,6]. This was added slowly not allowing the reaction temperature to increase to over 25°. The reaction was allowed to proceed for 72 hours. The excess lithium aluminum hydride was destroyed by adding 0.7 ml water, 0.7 ml 15% sodium hydroxide, and 2.4 ml water [8]. The solution was filtered and the organic layer extracted with ether, washed with water, and dried over calcium chloride. The ether was evaporated *in vacuo* and the residue distilled yielding 0.50 g (61% yield, 99% pure by vpc) of IIa, bp 68/1 mm; nmr (deuteriochloroform): δ 6.9-7.4 (m, 5H), 4.0-4.3 (m, 1H), 3.5-3.8 (m, 1H), 2.3-2.6 (m, 1H), and 1.5-2.1 (m, 4H); uv (cyclohexane): λ max 211.5 nm (ϵ 10,100), and a shoulder at 218.2 nm (ϵ 8420).

Anal. Calcd. for C₁₁H₁₂O: C, 82.46; H, 7.55; O, 9.99. Found: C, 82.41; H, 7.49; O, 9.94.

exo-6-Phenyl-2-oxabicyclo[3.1.0]hexane (IIb).

To a solution of 4.9 g of potassium *t*-butoxide in 25 ml of dry dimethyl sulfoxide, 1 gram of IIa is added. The solution was allowed to react for 72 hours a 60° under a dry nitrogen atmosphere [7]. The solution was then hydrolyzed, extracted with ether, washed with water and dried over calcium chloride. The ether was evaporated *in vacuo* and the residue distilled yielding 0.77 g (77% yield, 97% pure by vpc) of IIb, bp 118/9

mm; nmr (deuteriochloroform): δ 6.8-7.3 (m, 5H), 3.8-4.2 (m, 2H), 3.4-3.7 (m, 1H), and 1.6-2.2 (m, 4H); uv (cyclohexane): λ max 225.5 (ϵ 12,200).

Anal. Calcd. for C₁₁H₁₂O: C, 82.46; H, 7.55; O, 9.99. Found: C, 82.25; H, 7.36; O, 10.12.

Hydrogenation of *endo*-6-Phenyl-2-oxabicyclo[3.1.0]hexane (IIa).

A solution of 0.50 g of IIa in 50 ml of absolute ethanol was shaken with hydrogen over 0.1 g of 5% palladium on charcoal for 24 hours at 50 psi using a Parr hydrogenation apparatus [1,2]. The solution was filtered and the ethanol evaporated *in vacuo* yielding 0.50 g (99% yield) of a mixture of III and IV in a ratio of 6.22:1 respectively (determined by gas chromatography). Compound III was identified as 2-benzyltetrahydrofuran; nmr (deuteriochloroform): δ 7.1-7.3 (s, 5H), 3.5-4.2 (m, 3H), 2.5-3.1 (m, 2H), 1.3-2.1 (m, 4H). Compound IV was identified as 3-benzyltetrahydrofuran; nmr (deuteriochloroform): δ 7.0-7.3 (s, 5H), 3.3-4.0 (m, 4H), 1.3-2.7 (m, 5H).

Anal. Calcd. for III C₁₁H₁₄O: C, 81.44; H, 8.70; O, 9.86. Found: C, 81.21; H, 8.68; O, 9.95.

Anal. Calcd. for IV C₁₁H₁₄O: C, 81.44; H, 8.70; O, 9.86. Found: C, 81.35; H, 8.81; O, 10.06.

Hydrogenation of *exo*-6-Phenyl-2-oxabicyclo[3.1.0]hexane (IIb).

Hydrogenation of 0.50 g of IIb was carried out exactly as the hydrogenation of IIa yielding 0.49 g (97% yield) of a mixture of III and IV in a ratio of 1:2.27 (determined by gas chromatography).

Anal. Calcd. for III C₁₁H₁₄O: C, 81.44; H, 8.70; O, 9.86. Found: C, 81.33; H, 8.81; O, 9.88.

Anal. Calcd. for IV C₁₁H₁₄O: C, 81.44; H, 8.70; O, 9.86. Found: C, 81.37; H, 8.49; O, 9.71.

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