Introduction:

Pentaerythritol (2,2-bis-(hydroxymethyl)-1,3-propane-diol), 1, undergoes acid-catalyzed reaction with aromatic aldehydes (2 a-d) to give 3,9-diaryl-2,4,8,10-tetraoxaspiro[5.5]undecanes (3 a-d).

![Chemical Structure](image)

The products have interesting structures, and they serve to introduce the effects of conformation and symmetry upon NMR spectra. The $^{13}$C spectra and parts of the $^1$H spectra are easy to interpret, and examination of these compounds is particularly instructive when using Fourier transform NMR instruments.

PreLaboratory Exercise

Build structure 3 for your chosen substituent a, b, c, or d in Spartan and using a semiempirical method, calculate the relative energies of the spiroundecane system with the two aryl groups in the diequatorial, equatorial-axial and diaxial positions. Give a mechanism that explains how the more stable equatorial form can be formed exclusively.

Synthesis

Each team member will prepare a different spiro compound, the choice depending on the availability of the different aldehydes 2 a-d.

A 1/2” magnetic stirrer bar and 0.100 g (0.78 mmol) of pentaerythritol are placed in a reaction tube. To the tube is added 0.5 mL of glacial acetic acid, and an air condenser is attached. The reaction is heated and stirred until the solid is dissolved totally; the temperature of the contents is about 110°C when solution is complete. The condenser is removed, and 1.54 mmol of aromatic aldehyde is added. Without delay 0.2 mL of a 0.1 M solution of p-toluenesulfonic acid monohydrate in acetic acid is added. The condenser is reattached, and the mixture is heated and stirred for 60 seconds. (Longer reaction times lead to lower yields, and no product is isolated when the mixture is heated for 10 min.) The vessel is immediately placed in a bath of ice and water. After a few minutes crystallization is presumed to be complete and the solid product is separated by pipet filtration. The solid is washed with two to four drops of glacial acetic acid and then with three 2-mL portions of 0.1 M Na$_2$CO$_3$, with 2 mL of water, and 0.5 mL ethanol. The residue is recrystallized from toluene.

The products prepared using this procedure are 3,9-diphenyl-2,4,8,10-tetraoxaspiro[5.5]undecane (3 a), mp 157-158°C (reported (I), 159-160°C); 3,9-bis-(3'-methoxyphenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (3b), mp 125.5-127°C; 3,9-bis-(4'-methylphenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (3e), mp 200-202°C; or 3,9-bis-(3'-nitrophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (3d), mp 119-12°C.

Cleaning Up

The total amount of organic solvent waste (acetic acid, ethanol, and toluene) is 2-3 mL. These solvents can be combined with the first aqueous wash for hazardous waste disposal. The rest of the aqueous wash material can be
NMR Spectra of 3,9-Diary1-2,4,8,10-Tetraoxaspiro[5.5]Undecanes

We want to obtain NMR spectra on a 360 or 400 MHz NMR. $^1$H-NMR (300 MHz) and $^{13}$C-NMR (75 MHz) spectra have been reported by Clark using a General Electric QE-PLUS spectrometer. Chemical shifts are reported with respect to TMS, and, except where noted, samples were dissolved in CDCl$_3$.

Prove that the aryl substituents must occupy equatorial positions on the chair forms by using Spartan to calculate the relative energies of the diequatorial, equatorial-axial and diaxial diaryl spiroundecane system and show which is favored and that it is a rigid system(2). The median planes of the two chairs intersect, and a $C_2$ axis is present. The aryl groups are homotopic and therefore give just one set of NMR signals (3). C(3) and C(9) and their attached protons are likewise homotopic. Each methylene group is diastereotopic to the other one in its own ring and homotopic to one methylene group in the other ring. The four methylene groups, therefore, give two sets of NMR signals. In the discussion that follows, the spectra of 3c are discussed in some detail.

The $^{13}$C spectrum of 3c has nine signals: 21.4, 32.5, 70.7, 71.1, 102.4, 126.0, 129.1, 135.2, and 139.0. The last four are the signals produced by the sp$^2$ carbons and are in the range expected for the signals of aromatic carbons. The principle that proximity to electronegative atoms is deshielding allows one to assign the peak at 102.4 to C(3) and C(9) that are bonded to two oxygens; the peaks at 70.7 and 71.1 are the signals of the methylene carbons, and one of the high-field signals is produced by the spiro atom and the other by the methyl carbon. The methyl signal of toluene is at 21.3, 50 the highest-field signal is assigned to the methyl carbon. These assignments can be corroborated using APT and in DEPT spectra (4, 5).

Final Report

Read the original article and give a full discussion of the NMR spectra.