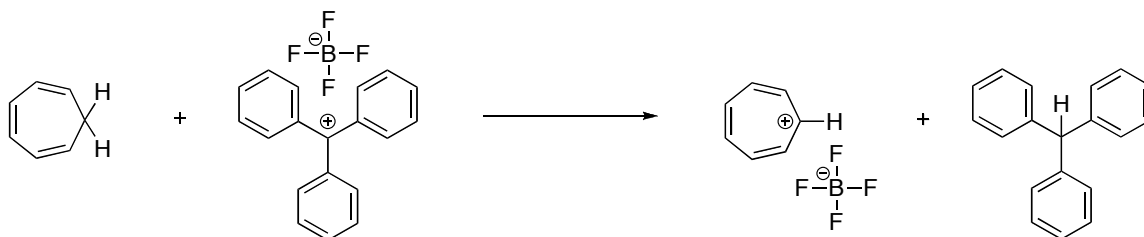
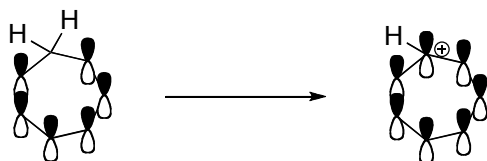


Tropylium Tetrafluoroborate: Synthesis of a Stable, Aromatic Cation



Introduction:

In 1891, G. Merling added bromine to cycloheptatriene to produce an unknown water stable salt.¹ It was not until 1954, that Doering and Knox unequivocally confirmed that the structure of the salt was indeed the cycloheptatrienyl cation.² The unusual stability of these salts results from the fact that in its cationic form the molecule is aromatic. According to Hückel's rule, in order for a molecule to be aromatic it must have $4n+2$ pi electrons which are in conjugation with one another. Cycloheptatriene contains an sp^3 carbon without an unhybridized p orbital, preventing delocalization of the pi electrons. Formation of the cation changes the hybridization from sp^3 to sp^2 creating an empty p orbital which allows for all six pi electrons to now be delocalized.



Experimental: (Note – Please perform all operations in a fume hood)

Weigh out 0.17 g (0.19 mL, 1.8 mmol) of cycloheptatriene and 0.6 g (1.8 mmol) of triphenylcarbenium tetrafluoroborate into a 50 mL round bottom flask with stir bar. Place flask on stir plate and begin to stir the solid mixture. Slowly add drop wise acetonitrile to the round bottom flask until all the solid material has gone into solution. It is important to use only the minimal amount of solvent necessary to solubilize all reagents. Once solution has formed wait approximately five minutes for reaction to go to completion. Once desired time has elapsed, remove the solvent on the rotovap. The dense white precipitate that forms is the tropylium

fluoroborate. Isolate the crystals by suction filtration and wash them using small portions of ice-cold ethanol (2 × 2 mL) followed by ice-cold diethyl ether (2 × 2 mL). Once the crystals have air dried, record the mass and acquire a UV-Vis spectrum of the sample.

Characterization

UV-Vis analysis:

λ 0.1N HCl 218 m μ (log ϵ 4.70), 274 m μ (log ϵ 3.61)

References:

¹ Merling, G. Chem. Ber. **1891**, 24, 3108.

² Doering, W. V. E.; Knox, L. H. J. Am. Chem. Soc. **1954**, 76, 3203.

³ Dauben, H. J.; Gadeckt, F. A.; Harmon, K. M.; Pearson, D. L. J. Am. Chem. Soc. **1957**,
79, 4557.

⁴ Conrow, K. Organic Syntheses, Coll. **1973**, 5, 1138.