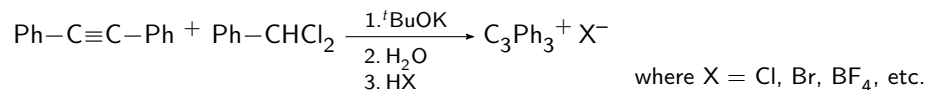


Preparation of an Aromatic Carbocation

Overview

In this project, you will prepare the aromatic triphenylcyclopropenyl carbocation and isolate it as either a halide or a fluoroborate salt:



The compound is simple to prepare, yet a fair number of transformations occur during the reaction and subsequent work-up. Your report, therefore, should include a detailed mechanism showing the conversion of tolan to the aromatic cation.

As this is essentially a one-step reaction, you should do more than just synthesize the compound. Two possibilities for enlarging the scope of the project follow, but you may also propose your own.

- *i.* Calculation of the HOMO-LUMO gap for the triphenyl cation and its trianisyl analog, *ii.* comparison of these gaps with UV-Vis spectra, and *iii.* rationalization of the λ_{max} difference between the two compounds. (Although Breslow provides spectra, you should also obtain one for your compound.)
- *i.* Calculation of (solvated) energies for Ar₃C₃OH and Ar₃C₃⁺ (Ar = Ph, anisyl), *ii.* estimation of pK_{R^+} values¹ for the two cations from these values, *iii.* rationalization of the difference between the two pK_{R^+} values, and *iv.* comparison of the calculated pK_{R^+} values with those obtained experimentally by Breslow. (For the purposes of this lab, a low level calculation — eg, AM1 — is fine.)

Notes on the Procedure

The reaction is straightforward. If the tBuOK appears goopy, it should be sublimed under vacuum before use. Use a small Erlenmeyer for this, not a sublimation apparatus, as the hot caustic will damage the glass.

Depending on availability, the carbocation may be precipitated by bubbling gaseous HBr or HCl through the dried extraction liquor (to give the bromide or chloride salt) or by addition of HBF₄ (fluoroborate salt).

The product is reasonably stable; nonetheless, it should be stored in a desiccator or under dry N₂. Do not recrystallize it: the recrystallization entails much loss. The crude product is sufficiently pure.

References

The references below may be obtained through the library's web-page. The 2.5 g scale on which the reaction is described is appropriate.

Preparation

Breslow, R.; Chang, H.W. *J. Am. Chem. Soc.* **1961**, *83*, 2367-2375.

Further Information

Breslow, R.; Yuan, C. *J. Am. Chem. Soc.* **1958**, *80*, 5991-5994.

¹ $pK_{R^+} = +\log K_{eq}$ for $\text{ROH} + \text{H}^+ \rightleftharpoons \text{R}^+ + \text{H}_2\text{O}$. Note that, due to the (+)-sign, a *positive* pK_{R^+} indicates a stable carbocation.