Synthesis and analysis of para-substituted phenylazo phosphonium dyes
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Abstract

Dyes are soluble molecules which possess a colour. There are many different dyes known, however, most dyes are azo dyes. Each azo dyes contains at least one azo group (R-N=N-R) and several subclasses are known. One subclass is the azobenzeneâ€™s (Ar-N=N-Ar), which colour is altered by changing the electron donating and withdrawing substituents on the aryl group. Most azobenzeneâ€™s are made of diazonium salts (R-N+≡N), which can be made from an alkyl or aryl amine. The active reagent NO+ is used during the synthesis, which is made from a nitrite. Alkyl diazonium salts are too unstable, therefore the focus is on aryl diazonium salts.

Another subclass of azo dyes are the azoimidazolium salts (Ar-N=N-NHC), which can be made from a diazonium salt and a N-heterocyclic carbene (NHC). As a phosphine, like a NHC, has a lone pair the same procedure can be followed forming phenylazo-phosphonium salts (Ar-N=N-P+R3). However, only two azophosphonium salts are known to be synthesised in this way.

For a class of azo dyes, the absorption in the UV-vis spectra is related to the Hammett sigma constant. This constant is a value for how electron donating or withdrawing a benzene substituent is. The more negative the value, how stronger donating the group is.

The first step of this project was the synthesis of six different para-substituted diazonium salts, which were recrystalised in acetone. In the second step, the six diazonium salts were reacted with tri-tert-butyl phosphine to synthesize para-substituted phenylazo-phosphonium salts with yields in the range of 55-94 %. These phenylazo-phosphonium salts do contain a impurity in the 31P{1H} NMR, which was identified as tetrafluoroborate tri-tert-butyl phosphonium.

The second part of the report contains an analysis of the 31P{1H} NMR and colour of the phenylazo-phosphonium dyes. There was a linear relation found between the 31P{1H} NMR shift and Hammett sigma constant of the functional groups, the higher the sigma constant, the higher the chemical shift.

All phosphonium salts possess colour and there seems to be a trend between the colour and Hammett sigma constant, however the phenyl- and acetoxy group do diverge too much which made the dataset too small. The consequence was that it was impossible to find a trend between the UV-vis absorption and sigma constant.

The synthesis of the para-hydroxy phenylazo-phosphonium salt was attempted. The recrystallisation of the diazonium salt in acetone was unsuccessful as the acetone reacted with the diazonium salt. Recrystallisation in ethanol and acetonitrile was performed, however the phenylazo-phosphonium salts still contained 20-25 % tetrafluoroborate tri-tert-butyl phosphonium as impurity and attempts to reduce it were unsuccessful.