

Photochemical Generation of an Acylium Ion Intermediate

Gou, H.; Mclelland, R. *University of Toronto, University of Victoria*

4-Cyanophenyl 2,6-dimethylbenzoate and its trimethyl analog were in an attempt to generate acylium ion intermediate through photochemical heterolysis. We employed two techniques in our study, HPLC and LFP. From our product analysis on the 2,6-dimethyl benzoate, we see the heterolysis route competes with the homolysis route to yield two charged species and a pair of radicals respectively (see figure below). One of the charged species, the acylium ion was quenched by water (and MeOH) to yield 2,6-dimethylbenzoic acid and methyl 2,6-dimethylbenzoate. The anion 4-cyanophenoxide was protonated to give 4-cyanophenol. The pair of radicals produced in the homolysis route were confined in a radical cage and reacted to give a photo-Fries product. From LFP data, we observed two transients. The One with $\lambda_{\text{max}} = 280 \text{ nm}$ is the 4-cyanophenoxide, which under the weakly acidic conditions of our experiment decayed by protonation. The appearance of the 4-cyanophenoxide within the laser pulse was consistent with a mechanism of photoheterolysis. The other transient had a λ_{max} of 330 nm. Various experiments showed that this transient is not a radical or triplet state intermediate, not the photo-fries intermediate, and it is probably not the acylium ion. However, there was not enough conclusive data for its identification. The conclusion of my experiments is that these esters do undergo photoheterolysis producing an acylium ion intermediate, even though this was not observed by LFP.

