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PHOTOHYDROLYSIS OF MONOSUBSTITUTED BENZOTRIFLUORIDES

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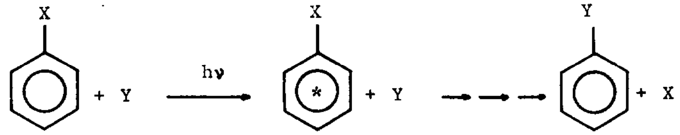
Light induced solvolysis reactions were first reported by HAVINGA and his coworkers in a series of classical papers (1). He showed that nucleophilic substitution reactions of type A are considerably accelerated when the reaction proceeds from the educt in its electronically excited state.

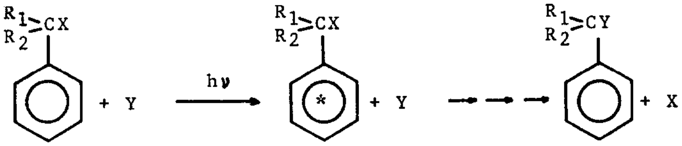
A



These results have been confirmed and extended by other research groups (2). (For a summary see ref. (3).)

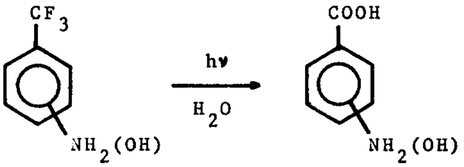
In an effort to obtain a more detailed insight into the mechanism of light induced substitution reactions of type B,

B



we have screened a series of donor-acceptor substituted benzene derivatives in view of their suitability for flash-photolysis experiments (4). These preliminary experiments have shown that donor substituted benzotrifluorides (BTF) are the compounds of choice.

In the course of these experiments we have observed that m-hydroxy-BTF and m-amino-BTF are exceptionally susceptible to photohydrolysis, yielding under the mild conditions described below (0.1 N hydrochloric acid and 2 N sodium hydroxide respectively) m-hydroxybenzoic acid (80 percent yield) and m-aminobenzoic acid (70 percent yield).



This is of interest for the following reason: both o-hydroxy-BTF and p-hydroxy-BTF (or p-amino-BTF) are hydrolysed in their electronic ground state to the correspondingly substituted benzoic acids in 1 N aqueous sodium hydroxide (cf. (5)) while their m-derivatives are stable even when refluxed in more concentrated alkaline solutions. The literature procedure (6) for their conversion to m-hydroxy- and m-aminobenzoic acid consists of the rather drastic method of heating the compounds in concentrated sulfuric acid. It is for this reason that we wish to report briefly on the photohydrolysis of the three isomeric hydroxy- and amino-BTFs.

The light induced hydrolysis of m-amino-BTF may serve as a typical example. 100mg m-amino-BTF are dissolved in 150 ml aqueous 2N sodium hydroxide. The solution is irradiated in a cylindrical vessel with the unfiltered light of a plunger type mercury high pressure lamp (Q 81, Quarzlampengesellschaft, Hanau) for 20 min at 20 ± 2°C. The solution is then buffered to pH = 4, and extracted with ether. The crude m-aminobenzoic acid so obtained is purified by chromatography and sublimation.

Under essentially identical conditions, but using 0.1 N aqueous hydrochloric acid as a solvent and irradiating for 45 min, m-hydroxy-BTF yields 80 percent m-hydroxy-benzoic acid.

Table I

Yields of Substituted Amino- and Hydroxybenzoic Acids after Irradiation of Correspondingly Substituted BTF's.

Substituent and Position	Solvent	Irradiation Time min.	Yield (100 = theory)
o-OH	0.1N HCl/H_2O	45	70
m-OH		45	80
p-OH		45	10
		360	0
o-NH_2	2N $NaOH/H_2O$	20	60
m-NH_2		20	70
p-NH_2		20	-

Remarks:

1) Under the conditions quoted for m-hydroxy-BTF, its isomer, o-hydroxy-BTF, reacts almost quantitatively to yield the corresponding acid. In contrast p-hydroxy-BTF yields mainly unidentified products in a slow reaction. m-Hydroxybenzoic acid is also formed from m-hydroxy-BTF in alkaline solutions.

2) Irradiation of the amino-BTFs in 0.1 N sodium hydroxide leads to secondary products which are absent if 2 N solvent is used. The p-isomer reacts even in the dark and only a minor acceleration is observed under irradiation.

3) The three isomeric methoxy-BTFs yield the corresponding methoxybenzoic acids if irradiated in 0.1 N hydrochloric acid under the same conditions as the hydroxy-compounds.

4) BTF with a nitrogroup in o, m or p position gives little or no reaction.

5) m-Chloro-BTF and p-chloro-BTF react sluggishly and do not yield the corresponding benzoic acids. The same is true for the three isomeric cyano-BTFs. On the other hand o-chloro-BTF yields o-hydroxybenzoic acid in a slow reaction.

6) BTF itself shows hardly any reactivity under the conditions described above. No benzoic acid has been isolated.

7) Test runs in non-aqueous solvents (dioxane, methanol, ether with 2 percent water) gave very low reaction rates and no identified products.

Finally, we would like to comment briefly on the mechanism of the light induced hydrolysis of the trifluoromethyl group. Flash photolysis experiments (4) using non degassed solutions in aqueous .01 to 1.0 N sodium hydroxide of the amino- and hydroxy-BTFs have shown that in the case of the o- and m-isomers the reactions proceed through intermediates, the lifetimes of which increase with decreasing pH of the solution. In particular, the intermediate formed from o-amino-BTF is long-lived enough at pH = 7 to be isolated. It was identified as o-aminobenzoylfluoride.

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