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THE PHOTOHYDROLYSIS OF EIGHT ISOMERIC TRIFLUOROMETHYLNAPHTHOLS[1)]

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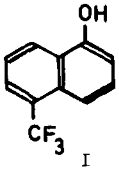
Light induced heterolytic solvolysis reactions of substituted benzene derivatives were first reported by HAVINGA, DE JONGH and DORST[2)]. Comparisons between the quantum yields of such reactions and reactivity indices obtained from simple model calculations for the excited state have been made by several authors[3)].
A related reaction is the photohydrolysis of the three isomeric hydroxybenzotrifluorides yielding the corresponding hydroxybenzoic acids[4)]. In order to increase the possible number of isomers (the correlation between theory and experiment thus being less subject to coincidence) we extended these studies to the title compounds which were obtained from the well known nitro- or methoxy-naphthoic acids by treatment with sulfur tetrafluoride followed by the usual aromatic substitution reactions.



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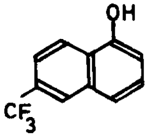

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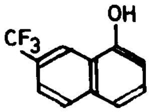

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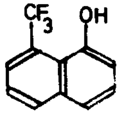

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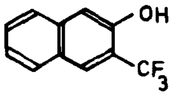

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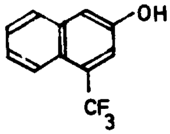

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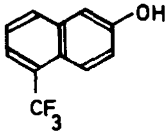

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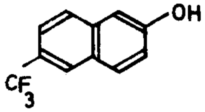
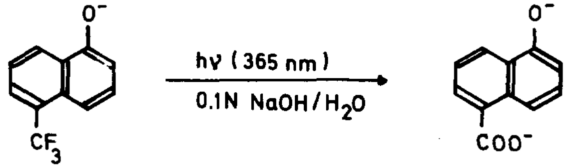


VIII

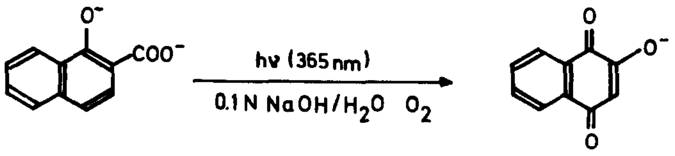
The photochemical behaviour of isomers I to VIII has been investigated by 365 nm irradiation of 10^{-4} molar solutions in nitrogen saturated, 0.1 N aequeous sodium hydroxide. Irradiation of isomers I to III and V to VII quantitatively yields the corresponding hydroxynaphthoic acids and isosbestic points are observed during the reaction.



(1)

Isomers IV and VIII do not show a clean reaction upon irradiation, the reaction products have not been identified. Nevertheless it seems important to note that IV undergoes chemical change with very high quantum efficiency, while VIII is almost inert towards light.

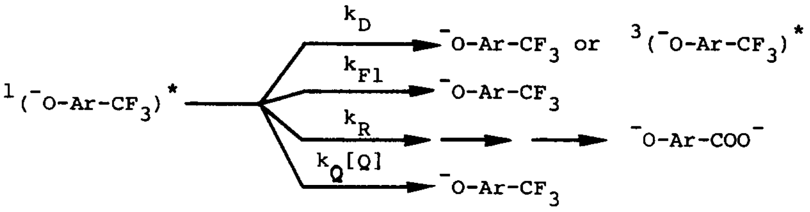
When aerated alkaline solutions of the trifluoromethylnaphthols are irradiated a consecutive and/or side reaction takes place yielding coloured products, presumably by photooxidation (compare ref. 5). In the case of 1-hydroxy-2-naphthoic acid the photoproduct was identified as 2-hydroxy-1,4-naphthoquinone.



(2)

The same product is formed when α-naphthol is irradiated in the presence of oxygen.

Stern-Volmer plots of the quenching of the quantum yields of reaction φ_R and of fluorescence φ_{Fl} by quenchers such as sodium sorbate, copper(II)-and iron(II)-sulfate give straight lines, the slopes deduced from quenching of φ_R and φ_{Fl} being equal within the limits of error. From this and the fact that the photoreaction could not be sensitized with acetone or triphenylene-1-sulfonic acid one may safely conclude6) that the photoreactive state of reactions (1) is the first excited singlet state S_1. The possible reaction paths of the excited molecules may thus be reduced to the following:



(3)

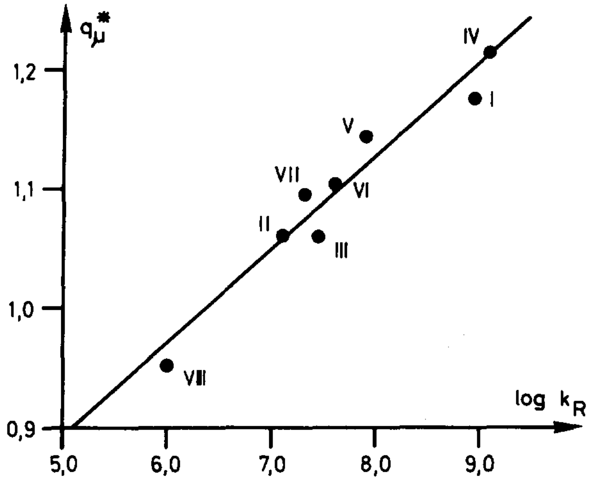
The rate constants shown in eq. (3) can be estimated by steady-state kinetic analysis[7].

Table: Absolute quantum yields φ_R, φ_{Fl} and reaction rates k_R in the first excited singlet state and π-charge density near the reaction center (explanation see below).

compound / data	I	II	III	IV	V	VI	VII	VIII
φ_R	.56 ±.07	.025±.002	.14 ±.01	(.7)	.71±.07	.50±.07	.27±.03	(< .01)
φ_{Fl}	.008±.003	.019±.005	.092±.02	.004±.002	.20±.02	.36±.04	.28±.03	.37±.04
$k_R \cdot 10^{-7} sec^{-1}$	90. ± 30.	1.3±.4	2.8±.6	(120.)	8.2±2.	4.2±1.1	2.1±.5	(<.1)
q^*_μ	1.176	1.062	1.061	1.215	1.144	1.104	1.097	.952

The charge densities q^*_μ of α- and β-naphtholate anion in the first excited state S_1 (μ referring to the ring carbon atom C_μ carrying the trifluoromethyl group) were calculated by a PARISER, PARR, POPLE SCF CI program with the parameters recommended by TICHY and ZAHRADNIK[8]. Charge densities from a simple Hückel calculation show a similar trend. As shown in the following figure the correlation between log k_R and q^*_μ is quite convincing. The same calculation for α- and β-naphthol can be used for an accurate description of the experimental band shifts of the first and second UV-absorption bands of the naphthols in cyclohexane caused by trifluoromethyl substitution in different positions[7]. This suggests that the shape of the potential surface of S_1 as predicted by the calculations seems to affect the rate of reaction significantly, although the primary photochemical step of the hydrolysis (a heterolytic C-F bond cleavage[4]) probably does not proceed entirely in the excited state.

Figure: Correlation between calculated charge densities and reactivities of the excited state S_1



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