Tetrahedron Letters No. 8, pp 685 - 686, 1972. Pergamon Press. Printed in Great Britain.

PHOTOREACTIONS OF AROMATIC COMPOUNDS XXIV [1]

NUCLEOPHILIC PHOTOSUBSTITUTION OF FLUOROBENZENE DERIVATIVES

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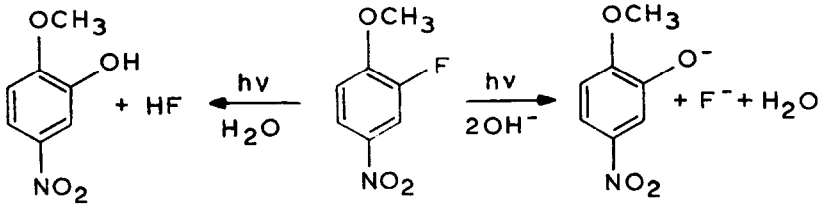
(Received in UK 7 January 1972; accepted for publication 19 January 1972)

In continuation of our work on aromatic photosubstitution we investigated the possibilities of the fluorine substituent as a leaving group[2].

When 500 mg of 3-fluoronitrobenzene in 1.5 l 1 N NaOH-solution (containing 2 % DMSO) were irradiated (Hanau TQ 81 mercury arc, pyrex filter) for 24 hours, 60 mg of 3-nitrophenol were obtained. The quantum yield of the reaction at 313 nm is 0.004 (10^{-4} M 3-fluoronitrobenzene; 10^{-1} M NaOH). The reaction can be sensitized with disodium-naphtalene-2,6-disulphonate: 10 mg of 3-nitrophenol were isolated from the irradiation mixture obtained from 500 mg of 3-fluoronitrobenzene and 20 mg of sensitizer in 1 l 0.1 N NaOH-solution (time of irradiation:5 hours).

Upon irradiation of 2- and 4-fluoronitrobenzene in alkaline solutions the corresponding phenols were isolated as the main products (minor products: azo- and azoxy-compounds). 2-Fluoromethoxybenzene reacted upon irradiation in NaOH- and HCL-solutions, yielding 2-methoxyphenolate and 2-chloromethoxybenzene, respectively. 3-Fluoro-4-methoxynitrobenzene in which the reactivity may be expected to be enhanced by the combined influence of the meta nitro and the ortho methoxy group, yields cleanly and efficiently 2-methoxy-5-nitrophenol as the sole product upon irradiation (Hanau TQ 81 mercury arc, pyrex filter) in alkaline solution. Even in acidic aqueous solutions irradiation results in substitution of the fluorine atom (See Fig.).



Quantum yields were deter mined in solutions having different pH-values: (λ= 313 nm; 7×10^{-5} M 3-fluoro-4-methoxynitrobenzene; solvent: 2 % CH_3CN/98 % H_2O).

ϕ= 0.11 at pH =3, ϕ= 0.11 at pH =7, ϕ= 0.50 at pH =12.

This is, to our knowledge, the first case in which a nitrobenzene derivative is so photoreactive that smooth substitution at a ring carbon atom can be effected by H_2O.

Other nucleophiles were also investigated (Table I).

Nucleophile	Solvent	Product
OH^-	98 % H_2O/2 % CH_3CN	2-methoxy-5-nitrophenolate
H_2O	98 % H_2O/2 % CH_3CN	2-methoxy-5-nitrophenol
H_2O	50 % H_2O/50 % CH_3CN	2-methoxy-5-nitrophenol (slow)
H_2O	25 % H_2O/75 % CH_3CN	none
H_2O	2 % H_2O/98 % CH_3CN	none
CH_3OH	CH_3OH	none
CH_3O^-	CH_3OH	3,4-dimethoxynitrobenzene
$C_2H_5O^-$	C_2H_5OH	3-ethoxy-4-methoxynitrobenzene
$C_3H_7O^-$	C_3H_7OH	4-methoxy-3-n-propoxynitrobenzene
$(CH_3)_2CHO^-$	$(CH_3)_2CHOH$	4-methoxy-3-i-propoxynitrobenzene
$(CH_3)_3CO^-$	$(CH_3)_3COH$	none

Table I. Photoreaction of 3-fluoro-4-methoxynitrobenzene with various nucleophiles.

In the absence of light the solutions of 3-fluoro-4-methoxynitrobenzene containing the various nucleophiles are completely stable.

The reaction of 3-fluoro-4-methoxynitrobenzene with hydroxide ion could almost completely be quenched by sodium sorbate; it can be sensitized with benzophenone. The quantum yield of the sensitized reaction at 254 nm is 0.085 (7×10^{-5} M 3-fluoro-4-methoxynitrobenzene; 1.24×10^{-4} M benzophenone; 10^{-2} M NaOH; solvent: 2 % CH_3CN/98 % H_2O; nitrogen atmosphere). The presence of oxygen lowers the efficiency of sensitization. Significantly, 3-fluoro-5-methoxynitrobenzene, affords 3-fluoro-5-nitrophenolate upon irradiation in alkaline solution, in conformity with other 3-substituted meta-methoxynitrobenzenes[3,4]; no substitution of fluorine was observed.

References

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