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AN AROMATIC PHOTONITRATION[1]

Christopher S. Foote[2a], Paul Engel[2b], and Thomas W. Del Pesco[2b]
Contribution No. 1823 from the
Department of Chemistry, University of California
Los Angeles, California 90024

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Recent interest in photochemical aromatic substitution reactions[3] and in photochemical reactions of nitro compounds[4] prompts us to report some observations of photochemical aromatic nitration. A dilute solution of nitrobenzene in 70% HNO_3 was continuously purged with purified N_2 and irradiated with light from a Hanovia 550 W medium pressure Hg arc. Wavelengths below 3660Å were removed by a filter solution, so that only the 3660Å line was absorbed by nitrobenzene; HNO_3 is transparent at this wavelength. Nitrobenzene undergoes no detectable reaction under these conditions in the dark. The principal products of the photochemical reaction are p- and m-dinitrobenzenes and picric acid, in amounts which depend strongly on the exact conditions and on the time of irradiation. Typically each is produced in roughly 20% yield, but the proportions are not reproducible; only about 60% of the starting material is accounted for. The reaction course is dependent on the amounts of nitrogen oxides present: addition of urea or potassium sulfamate (which remove nitrogen oxides) increases the proportion of p-dinitrobenzene substantially. Runs in which the concentration of nitrogen oxides was allowed to build up by interrupting the N_2 purge gave increased proportions of the m-isomer. The lack of reproducibility of the runs in pure HNO_3 is understandable, since nitrogen oxides (which absorb light at 3660Å) are produced during the reaction and the purging rate was difficult to reproduce. The runs with added urea gave the most reproducible product distributions. The effects of the experimental variables are shown in Table I.

TABLE I

Effect of Reaction Conditions on Product Composition

(0.004M Nitrobenzene in 70% HNO_3)

Added Material	Products (%)				
	Dinitrobenzenes[a]			Picric Acid[b]	Unreacted Nitrobenzene[a]
	o	*m*	*p*		
0.07M Urea	2.5	9	19	20	9
0.005M $KOSO_2NH_2$	c	13	14	31	10
———	c	23	19	c	c
N_2 Purge Interrupted	1	11	5	11	32

a Determined gas chromatographically, using internal standard.
b Determined spectrophotometrically on an extract. These are minimum values, as extraction was not quite complete.
c Not determined.

Two further observations are relevant to an understanding of this reaction. 1) No deuterium is introduced into nitrobenzene on irradiation in D_2O/D_2SO_4 mixtures, as shown by mass spectroscopy of recovered nitrobenzene. 2) Although benzonitrile is transparent at 3660Å, and undergoes negligible thermal or photochemical reaction in HNO_3 by itself or with added $NaNO_2$ (to produce nitrogen oxides), irradiation of solutions containing both nitrobenzene and benzonitrile produces *m*-nitrobenzonitrile, along with the products derived from nitrobenzene.

While speculation about the detailed mechanism of these obviously complex transformations would be premature, the following points can be made.

1. The lack of deuterium incorporation suggests that the nitration is not an electrophilic substitution on an excited state of nitrobenzene, a possibility which originally appeared attractive.

2. The formation of *m*-nitrobenzonitrile suggests that either a reactive nitrating (or nitrosating) agent is present in the solution, or else benzonitrile is activated for nitration by energy transfer from nitrobenzene.

3. At least some of the *m*-dinitrobenzene is formed in a process which requires the presence of nitrogen oxides in the solution.

4. Since photolysis of nitrobenzene in the vapor phase (although at much shorter wavelengths) has been reported to produce nitrosobenzene and *p*-nitrophenol,[5] these products might account for at least some of the production of *p*-dinitrobenzene and picric acid.[6] Alternatively, phenyl nitrite could be formed from nitrobenzene photochemically, by analogy with work of Chapman,[4e] and this could give picric acid. Several other processes could account for the formation of *p*-dinitrobenzene, but futher work will be necessary to decide among the possibilities.

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2. (a) A. P. Sloan Fellow; (b) N.S.F. Undergraduate Summer Research Participant.

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