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PHOTOCHEMICALLY INDUCED REACTIONS OF 4-NITROANISOLE

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In view of recent reports of photoinduced substitution reactions of nitroaromatics,[1-4] we are prompted to report our preliminary results regarding the photochemical reactivity of 4-nitroanisole[5] in acetonitrile and benzene solvent systems. 4-Nitroanisole is stable in these solvents in the dark and at elevated temperatures for prolonged periods. However, upon irradiation of degassed solutions ($\geq 10^{-3}$ M) with the full light of a 450-watt Hanovia mercury arc lamp using a Pyrex filter the slow conversion to 2-nitro-4-methoxyphenol and 4-nitrosoanisole was observed. The reaction was conveniently followed by monitoring the increasing absorbances at 395 mμ and 730 mμ respectively, due to formation of the two products. Isolation and characterization of the photoproducts by spectroscopic techniques showed them to be identical with independently prepared samples. Under identical photolysis conditions 2-nitroanisole and 3-nitroanisole were found unreactive and only starting material could be isolated after prolonged periods (ca 200 hours).

Product distributions obtained from degassed irradiations of various concentrations of 4-nitroanisole in acetonitrile were observed to be independent of the concentration of starting material. Disappearance of starting material was monitored and clearly indicated two mole equivalents of 4-nitroanisole were consumed with equimolar amounts of 2-nitro-4-methoxyphenol and 4-nitrosoanisole being formed. Each of these two products were formed with the same quantum efficiency, 2.3×10^{-3}. Clean isosbestic points were observed in all cases. Analysis of the gaseous products evolved during photolysis indicated the presence of trace amounts of nitrogen (II) oxide and nitrous oxide with no trace of nitrogen dioxide or oxygen being evolved. Absence of

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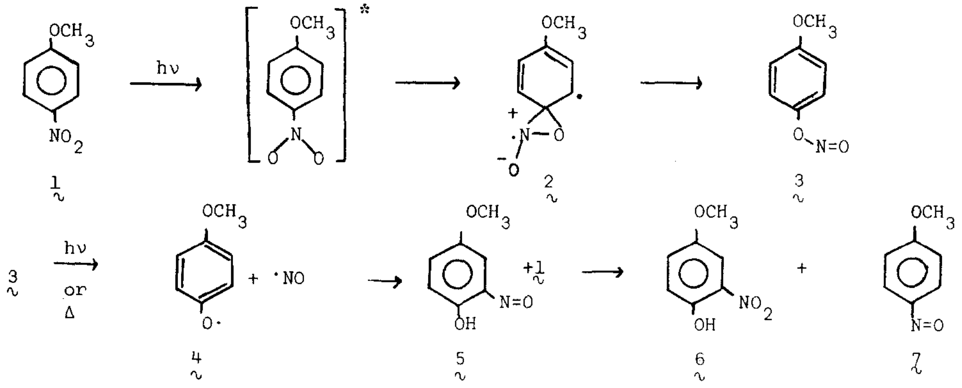
nitrogen dioxide is consistent with the proposed rearrangement of nitroaromatics to aryl nitrites under photochemical conditions.[6] No other products could be detected other than trace amounts of the bis-(4-methoxyphenyl)-nitroxide stable free radical (by ESR) produced by further reaction of the 4-nitrosoanisole under photolysis conditions.[7]

Sensitization and quenching studies indicate that the rearrangement of 4-nitroanisole proceeds via a triplet excited state. Triphenylene (E_T = 67 kcal/mole) cleanly sensitizes the reaction while biacetyl (E_T = 55 kcal/mole) and anthracene (E_T = 42 kcal/mole) are totally ineffective. Phosphorescence studies indicate that 4-nitroanisole has a triplet energy of 60.8 kcal/mole.[8] Nitric oxide, which is known to be an effective triplet quencher, completely suppresses the rearrangement reaction. Molecular oxygen does not appear to quench the reaction, but it does affect the stoichiometry. Irradiation in the presence of bubbling oxygen increased the amounts of 2-nitro-4-methoxyphenol relative to 4-nitrosoanisole (inert to photooxidation by oxygen).

On the basis of these experimental results we are prompted to propose the following mechanistic sequence to account for the observed photochemical conversion of 4-nitroanisole.



Photoinduced rearrangement of 1 produces 3 which cleaves to 4 and nitric oxide. The phenoxy radical 4 reacts with nitric oxide to afford 5 which undergoes further oxidation by 4-nitroanisole to yield 6 and 7. Attempts at isolation or identification of the intermediate 5 from irradiated solutions of 4-nitroanisole were unsuccessful as were all attempts at synthetic preparation. The unusual reactivity of 5 to further oxidation is apparently due to the meta-methoxyl substituent. Consistent with this is our observation that irradiation of 1-methoxy-4-nitronaphthalene produces 2-nitro-4-methoxynaphthol and 1-methoxy-4-nitrosonaphthalene in a 1:1 ratio while 1-nitronaphthalene upon irradiation yields only 2-nitrosonaphthol.

The oxidation of **5** to **6** in rigorously degassed solutions apparently occurs via a bimolecular oxygen transfer from **1** to **5** probably via a thermal process. The observed decreases in the amount of 4-nitrosoanisole formed in irradiations under bubbling oxygen apparently arise from competition for oxidation of **5** by **1** and molecular oxygen.

Further studies to delineate the scope and mechanistic implications of this rearrangement are currently in progess.

REFERENCES

1. E. Havinga, R.O. de Jongh, and M.E. Kronenberg, *Helv. Chim. Acta*, **50**, 2550 (1967) and references cited therein.
2. R.L. Letsinger and O.B. Ramsay, *J. Amer. Chem. Soc.*, **86**, 1447 (1964).
3. E. Havinga, R.O. de Jongh, and W. Dorst, *Rec. Trav. Chim.*, **75**, 378 (1956).
4. R.L. Letsinger and K.E. Steller, *Tetrahedron Lett.*, 1401 (1969).
5. Formation of 2-nitro-4-methoxyphenol from irradiated 0.10N NaOH solutions of 4-nitroanisole has been classified as arising from a possible photosubstitution process; see, S. de Vries and E. Havinga, *Rec. Trav. Chim.*, **84**, 601 (1965).
6. O.L. Chapman, D.E. Heckert, J.W. Reasoner, and S.P. Thackaberry, *J. Amer. Chem. Soc.*, **88**, 5550 (1966); C. Kaneko, I. Yokoe, and S. Yamada, *Tetrahedron Lett.*, 775 (1967).
7. A. Mackor, Th.A.J.W. Wajer, Th. J. de Boer, and J.D.W. van Voorst, *Tetrahedron Lett.*, 2115 (1966).
8. L.B. Jones and J.C. Kudrna, unpublished results.