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Photochemical Nucleophilic Substitution Reactions of Methyl Substituted Derivatives of *p*- and *o*-Nitroanisole[1]

Masaki Sawaura and Toshio Mukai*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980

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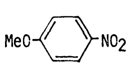
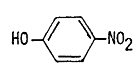
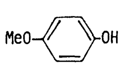
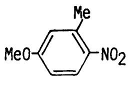
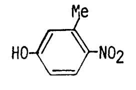
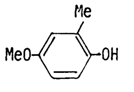
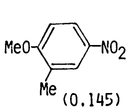
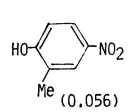
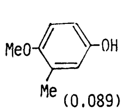
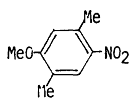
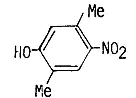
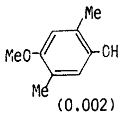
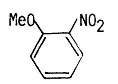
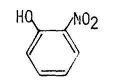
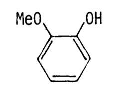
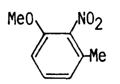
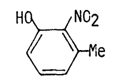
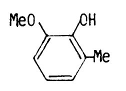
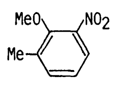
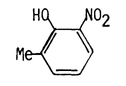
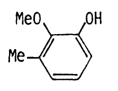
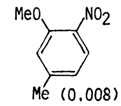
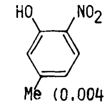
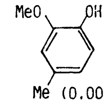
Synopsis. Photosubstitution reactions of several methyl substituted derivatives of *p*- and *o*-nitroanisole with hydroxide ion were investigated. The methyl substituent seemed to show an uncertain (probably electronic) effect in addition to the steric effect for the replacement of both the methoxy and the nitro groups. Mainly, the replacement reaction of the nitro group is discussed.

It is well known that aromatic nucleophilic substitution reactions take place differently in the ground state and in the excited state.[2] Theoretical calculations[3] support the sharp contrast between them.[4] In the photosubstitution reaction of *m*-nitroanisole with hydroxide ion, *m*-nitrophenol was produced as a single product as was expected from the orientation rule that the nitro group activates the replacement at the meta-position.[5] However, with *o*- and *p*-nitroanisoles the meta-orientation rule is not useful for the prediction of the product. For instance, Letsinger[6] and Havinga[7] independently studied the photosubstitution reactions of *p*- and *o*-nitroanisoles (**1** and **5**) with hydroxide ion and obtained *p*- and *o*-methoxyphenols (**1b** and **5b**) in addition to *p*- and *o*-nitrophenols (**1a** and **5a**). The formation of **1b** and **5b** could be explained by the orientation rule that the methoxyl group activates at the *o*- and *p*-positions.[7] However, it has not been rationalized why methoxyl group at para or ortho positions of the nitro group is replaced and why the product ratios (**1a**/**1b** and **5a**/**5b**) are inverted in the *o*- and *p*-isomers (see Table 1). Dudell's study on the flash photolysis of **1** and **5** showed that **1a** and **5a** were formed from the triplet states,[8] but no clear explanation has been made on the reaction machanism. In order to gain an insight into the reaction mechanism, we studied the methyl substituent-effect on the replacement of the nitro- and the methoxyl group in the derivatives, **2**—**4** and **6**—**8**, with hydroxide ion. An expectation is that the ortho-substituted methyl group should supress more effectively the π-π^* excitation than the n-π^* excitation of the nitro group, thus resulting in decrease in the replacement of the methoxyl group.

Table 1. Quantum yields[a)] for the depletion of the reactants (**1**—**8**)and for the formation of the products (**1a**, **1b**—**8a**, **8b**)

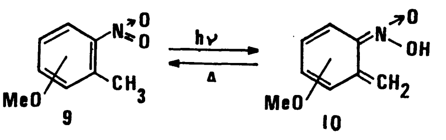
REACTANT(-Φ)		PRODUCTS(Φ)			
1	 (0.111)	1a	 (0.020)	1b	 (0.091)
2	 (0.005)	2a	 (0.005)	2b	 (0.000)
3	 (0.145)	3a	 (0.056)	3b	 (0.089)
4	 (0.005)	4a	 (0.003)	4b	 (0.002)
5	 (0.028)	5a	 (0.022)	5b	 (0.006)
6	 (0.003)	6a	 (0.003)	6b	 (0.000)
7	 (0.044)	7a	 (0.044)	7b	 (0.000)
8	 (0.008)	8a	 (0.004)	8b	 (0.004)

a) The quantum yields during the initial stage (less than 5 min) of the substitution reactionsare shown here. Side reactions appeared after prolonged irradiation.

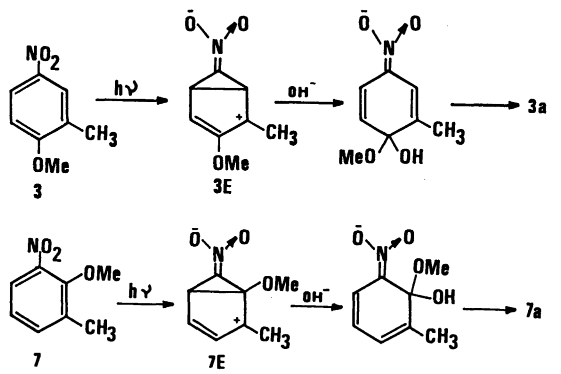
Results and Discussion

The methyl substituent-effect on the photosubstitution reactions of **1**—**8** is discussed on the basis of the quantum yields shown in Table 1. The introduction of a methyl group at a position next to the nitro group, as in **2** and **6**, resulted in a great retardation of the replacement of both the methoxyl and the nitro groups. Neither **2b** nor **6b** were detected and **2a** and **6a** were formed only in poor yields. Decrease in the reactivity of **2** and **6** is clearly to be ascribed to the steric effect of the methyl group that inhibits the coplanarity of the nitro group and the phenyl moiety (see the UV spectra).[9] The methyl group also prevents the attack of hydroxide ion to the nitro group. In addition to these effects, the photo-valence isomerization between the nitro-form (**9**) and the aci-form (**10**) should become a main decay process in the excited state of **2** and **6**. When **2** was irradiated in dioxane containing deuterium oxide, incorporation of deuterium was found to take place in the methyl group.

With **3** and **7**, the introduction of the neighboring methyl group led to the rapid formation of **3a** and **7a**.



Compared with **1** and **5** the more sterically hindered methoxyl group was replaced more easily by hydroxide ion. This can be rationalized by the stabilization of the excited states, **3E** and **7E**, by the methyl substituent meta to the nitro group as shown in the following scheme.[11]



Contrary to this, the replacement of the nitro group in **3** and **7** seemed to be retarded very little by the methyl group located ortho to the methoxyl group.

The substitution reaction of 5-methyl-2-nitroanisole (**8**) was found to occur at a slow rate, even though the methyl group is not present at the positions next to the nitro and the methoxyl groups. The formation of **8b** was not affected by the methyl substituent, but that of **8b** was retarded compared to the formation of **5a**. However, this retardation could not be accounted for by the methyl substitution present.[12] Thus, it can be concluded that the methyl group enhances the replacement of the ortho-substituted methoxyl group in *m*-nitrotoluene derivatives such as **3** and **7**, but it retards the replacement of the para- or ortho-substituted methoxyl group in *o*- and *p*-nitrotoluene derivatives **2**, **6**, and **8**.

In the photosubstitution reaction of 2,5-dimethyl-4-nitroanisole (**4**), products **4a** and **4b** were obtained in poor yields. It is difficult to predict how methyl groups affect the substitution reaction of **4**, but the effect of the methyl group ortho to the nitro group seems to be stronger than that of the methyl group meta to the nitro group.

Experimental

Materials. Methyl derivatives of nitroanisole were prepared according to the literature[13—16] and identified by their mp and spectral data.

Measurements. A spectro-photofluoromenter Hitachi MPF-4 [xenon monochromatic light (UXL-150D)] was used as the light source for the irradiation. Absorption spectra were measured with a Hitachi 340 spectrophotometer. The quantum yields were obtained by using the potassium tris-oxalatoferrate(III) chemical actoinmeter.[17] A solution (1×10^{-4} mol/dm^3) of *p*-nitroanisole (**1**) in a mixture of *t*-butyl alcohol and water (1 : 3) containing 0.2 mol/dm^3 sodium hydroxide was irradiated with monochromatic light (at 313± 20 nm) in a quartz cell under nitrogen atomsphere. The absorption maximum of *p*-nitrophenol (at 420 nm, $\varepsilon=20700$) was used for the reference and the quantun yield of the formation of **1a** was measured spectroscopically based on the absorption coefficient at 420 nm. The UV spectrum of this reaction mixture corresponded well with a spectrum calculated for a mixture of 82% of *p*-methoxyphenol and 18% of *p*-nitrophenol (see report by Letsinger *et al.*[6]). On the other hand, the isolation of photoproducts, **1a** and **1b**, was carried out in preparative scale experiments. The photoreactions of other derivatives (**2**—**8**) were monitored in the same way as mentioned above and the quantum yields shown in Table 1 were thus obtained.

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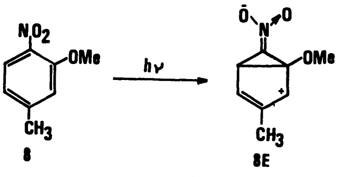
9) The absorption maximum and coefficient of **1**, **2**, **5**, and **6** are herein cited: **1**, $\lambda_{\max}=316$ nm ($\varepsilon=10000$), **2**, $\lambda_{\max}=313$ nm ($\varepsilon=8000$), **5**, $\lambda_{\max}=333$ nm ($\varepsilon=3500$), **6**, $\lambda_{\max}=310$—350 nm ($\varepsilon=650$—450, sh).

10) H. Morrison and B. H. Migdalof, *J. Org. Chem.*, **30**, 3996 (1965).

11) Such a stabilization effect at a cation site by the methyl group can be found in the photoreactions of santonine and its related compounds. See. K. Schaffner, *Adv. Photochem.*, **4**, 81 (1966).

12) The methyl substituent does not affect the stability of the excited state, **8E**. Compare **8E** with **3E** and **7E**.



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