

**SUBSTITUENT EFFECTS IN AROMATIC PHOTOCHEMISTRY.
UV IRRADIATION OF 3,4-DIMETHOXYBENZONITRILE AND
3,4-DIMETHOXYACETOPHENONE IN THE PRESENCE OF
INORGANIC ANIONS**

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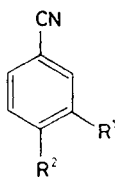
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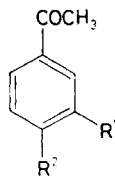
Ultraviolet photolysis of 3,4-dimethoxybenzonitrile (*Ia*) and 3,4-dimethoxyacetophenone (*IIa*) in the presence of the hydroxide or cyanide anion leads to nucleophilic displacement of either the *para* or the *meta* methoxy substituent. The ratio of isomeric photoproducts is dependent upon the nature of the nucleophile. Photoreactions with the OH^- anion lead exclusively to the substitution at C-3. On the other hand, both isomers are formed when acetophenone *IIa* is irradiated in the presence of CN^- , with the C-3/C-4 substitution ratio 3 : 2. In the case of the photocyanation of *Ia*, the C-4 substituted product dominates, the C-3/C-4 ratio ranging from 1 : 2 to 1 : 6 in dependence on the nucleophile concentration. These differences between the OH^- and CN^- anions are related to the results of a fluorescence quenching study which has revealed that only the latter nucleophile interacts with singlet-excited substrates. A non-linear Stern-Volmer plot was observed for the quenching of the second excited state of *Ia* by the cyanide anion. This indicates several distinct quenching modes, in relation to the concentration dependence of regioselectivity. The activating power of $-\text{H}$, $-\text{CN}$, $-\text{COCH}_3$, and $-\text{NO}_2$ substituents, as measured by relative quantum yields of disappearance for 3,4-dimethoxy-R-substituted benzenes, is 1 : 2.5 : 5 : 580 and 1 : 1.5 : 6 : 1 000 in their photoreactions with OH^- and CN^- anions, respectively.

Starting from the early observations by De Jongh of an accidental photohydrolysis of some nitrophenyl esters^{1,2}, the experimental data concerning structure-reactivity relationships in the nucleophilic aromatic photosubstitution ($\text{S}_{\text{N}}\text{Ar}^*$) began to accumulate. In the mid-seventies, several reviews appeared^{3,4} in which substituents were classified according to their orientation effects. One of the empirical rules stated that strong electron acceptors generally exhibit an activating and *meta*-orienting influence upon the course of the $\text{S}_{\text{N}}\text{Ar}^*$ reactions, despite of the fact that the only substituent of that class investigated in detail was the nitro group. The *meta*-selective photohydrolysis of 3,4-dimethoxy-1-nitrobenzene³ (*III*) can serve as example of an excited-state reversal of the orientation effect in comparison with the ground state of the same molecule. It has long been known⁵ that there is a parallelism between the $-\text{NO}_2$ and $-\text{CN}$ substituents in thermally activated $\text{S}_{\text{N}}\text{Ar}$ reactions. On the other hand, the only report concerning photosubstitution reactions of benzonitrile

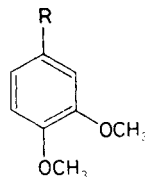
derivatives is a remark by Van Riel and coworkers⁶ that "similar methoxysubstituted benzonitriles exhibited much slower reactions with the lack of selectivity". In this respect, the validity of the orientation rule mentioned above is probably less general than it claims. It is nevertheless alleged in several organic photochemistry textbooks that, as for the directing effects in nucleophilic aromatic photosubstitution, the cyano and nitro substituents behave much the same⁷.



I



II

III, R = NO₂

IV, R = H

V, R = CHO

In formulae I and II: *a*, R¹ = OCH₃; R² = OCH₃
b, R¹ = OH; R² = OCH₃
c, R¹ = OCH₃; R² = OH
d, R¹ = CN; R² = OCH₃
e, R¹ = OCH₃; R² = CN

In order to elucidate these discrepancies we undertook a study of the photochemical behaviour of the title compounds *Ia* and *Iia* which are structurally related to the thoroughly studied^{3,8} nitrobenzene derivative *III*. It was the aim of the present work to answer the following two questions. First, whether there is an overall activation effect of the —CN and —COCH₃ substituents as measured by the quantum yields relatively to the unsubstituted reference substrate *IV*, and second, what are the orientation effects of these substituents as measured by the product distribution. Besides, it was decided to employ two different anionic species since pronounced differences in S_NAr* reactivity are commonly encountered depending on the nature of the nucleophile³.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. High-resolution mass spectra were taken on an AEI MS-902 spectrometer, electron energy 70 eV, source temperature 150–250°C. ¹H NMR spectra were measured with a Varian XL-200 instrument in deuteriochloroform using tetramethylsilane as an internal standard. Chemical shifts are given in δ and the interaction constants in Hz. UV spectra were measured with a Varian Cary 219 spectrophotometer in methanol, spectral band-width 1.5 nm. Fluorescence spectra were recorded on a Fluorolog 2 (SPEX Industries) spectrofluorimeter equipped with a 450 W xenon lamp, double emission

and excitation monochromators (linear reciprocal dispersion 1.8 nm/mm) and a cooled R 928 photomultiplier tube, slits 0.5 mm, scan rate 0.5 nm/s. Data reduction and smoothing were accomplished with the SPEX Datamate using standard algorithms.

Flash-chromatographic separations were achieved on a 3 × 30 cm column of 30–60 μm silica gel deactivated with 15% (w/w) of water. Thin-layer chromatography was run on Silica Woelm G-DC plates, elution with light petroleum–ether (4 : 1) or light petroleum–benzene–acetone (10 : 10 : 1 v/v). Preparative TLC was performed on Merck type 60 silica gel GF-254. HPLC analyses were performed on a 0.4 × 15 cm column of Separon SI C-18 modified silica gel (Laboratorní přístroje, Prague, particle size 5 μm), elution with methanol–water 60 : 40, flow rate 0.4 ml/min with the UV detection at 254 nm. GLC analyses were run with a Beckman GC-65 type instrument on a 0.4 × 150 cm column of 3% OV-17 on Gas-Chrom Q, oven temperature 200 to 300°C.

Tert-butanol was distilled prior to use. Water was distilled from potassium permanganate. The preparation of potassium cyanide and deoxygenation of nitrogen gas was described elsewhere⁸.

Syntheses of the Starting Compounds and Expected Photochemical Products

3,4-Dimethoxybenzonitrile (*Ia*) was prepared from the corresponding aldehyde by the reaction with hydroxylamine hydrochloride in boiling dimethylformamide⁹ and was twice crystallized from ether–hexane, yield 76%, m.p. 67.5–68°C, ref.¹⁰ m.p. 67°C. 3-Hydroxy-4-methoxybenzonitrile (*Ib*), yield 68%, m.p. 130–132°C (ether–hexane), ref.¹⁰ m.p. 128–129°C, and 4-hydroxy-3-methoxybenzonitrile (*Ic*), yield 78%, m.p. 88°C (ether–hexane), ref.¹⁰ m.p. 87°C, were obtained by the same method. 4-Hydroxy-3-methoxyacetophenone (*Iic*), yield 70%, m.p. 113–115°C (water), ref.¹¹ m.p. 115°C. 3-Hydroxy-4-methoxyacetophenone (*Iib*), yield 45%, m.p. 92°C (benzene), ref.¹² m.p. 91–92°C.

3-Cyano-4-methoxyacetophenone (*IId*) was synthesized from 3-amino-4-methoxyacetophenone¹³ by the Sandmeyer reaction in a modification according to Bergmann¹⁴, yield 68%, m.p. 156 to 156.5°C (hexane–ether). For C₁₀H₉NO₂ (175.1) calculated: 68.56% C, 5.18% H; found: 68.62% C, 5.16% H. High-resolution mass spectrum: calculated 175.0633; found 175.0641. ¹H-NMR spectrum: 2.58 (s, COCH₃), 4.02 (s, OCH₃), 7.68 (d, H-5, *J*(5, 6) = 8.6), 8.20 (m, H-2, H-6). UV spectrum: λ_{max} 300 nm (ε 130 m² mol⁻¹), 264 (510), 221 (1 000).

4-Cyano-3-methoxyacetophenone (*IIE*) was prepared from 4-amino-3-methoxyacetophenone¹⁵ by the same method¹⁴, yield 57%, m.p. 110–112°C from hexane. For C₁₀H₉NO₂ (175.1) calculated: 68.56% C, 5.18% H; found: 68.48% C, 5.23% H. High-resolution mass spectrum: calculated 175.0633; found 175.0639. ¹H NMR spectrum: 4.01 (s, OCH₃), 2.64 (s, COCH₃), 7.68 (d, H-5, *J*(5, 6) = 8.2), 7.55 (dd, H-6, *J*(6, 5) = 8.2, *J*(6, 2) = 1.4), 7.56 (d, H-2, *J*(2, 6) = 1.4). UV spectrum: λ_{max} 320 nm (ε 300 m² mol⁻¹), 252 (880).

Preparative Photolyses

The aromatic substrate (*Ia* or *Iia*) was dissolved in tert-butanol (100 ml) and the solution was mixed with water (300 ml). Potassium cyanide or potassium hydroxide was added, the mixture was deoxygenated with a stream of nitrogen (30 min) and subsequently irradiated in a preparative immersion-well photoreactor (Fritz GmbH) using a low-pressure mercury lamp Hanau TNN-15. A continuous stream of nitrogen was introduced during the irradiation period. At regular time intervals, samples were taken off and were analyzed by means of GLC using tetradecane as an internal standard; conversion of the starting material was calculated from the integrated peak

areas. The reaction mixture was acidified with concentrated hydrochloric acid, saturated with sodium chloride and the separated aqueous layer was extracted with tert-butanol (2 × 50 ml). Organic extracts were diluted with chloroform (150 ml), dried with anhydrous magnesium sulphate and evaporated *in vacuo*. When necessary, products were isolated by repeated flash chromatography and were purified by preparative TLC and/or crystallization.

Photohydrolysis of Ia. 3,4-Dimethoxybenzonitrile (*Ia*) (163 mg, 1.00 mmol) and potassium hydroxide (4.68 g, 0.083 mol) were irradiated for 8 h (14% conversion). TLC, GLC, and HPLC analyses of the crude photolyzate after the usual workup indicated the presence of 3-hydroxy-4-methoxybenzonitrile (*Ib*) and 3,4-dimethoxybenzaldehyde (*V*) identified by comparison with authentic samples. Quantitative analysis was performed by HPLC using benzene as an internal standard.

Photocyanation of Ia. 3,4-Dimethoxybenzonitrile (*Ia*) (163 mg, 1.00 mmol) and potassium cyanide (2.08 g, 0.032 mol) were irradiated for 9 h (10% conversion). The crude reaction mixture from five identical experiments and after the usual workup was subjected to flash column chromatography, elution with light petroleum–benzene–acetone (10 : 10 : 1). 2,5-Dicyano-1-methoxybenzene (*Ie*) was eluted first and was crystallized from methanol, m.p. 208–210°C, ref.¹⁶ m.p. 205–206°C. ¹H NMR spectrum: 7.68 (d, H-5, *J*(5, 6) = 7.8), 7.33 (dd, H-6, *J*(6, 5) = 7.8, *J*(6, 2) = 1.3), 7.23 (d, H-2, *J*(2, 6) = 1.3). UV spectrum: λ_{\max} 318 nm (ϵ 535 m² mol⁻¹). 253 (1 680), 215 (? 250). Further elution gave a mixture of the unreacted *Ia* and 2,4-dicyano-1-methoxybenzene (*Id*) which was isolated by column chromatography using light petroleum–ether (1 : 1) and purified by preparative TLC, m.p. 204–205°C (hexane–ether). For C₉H₆N₂O (158.2) calculated: 68.35% C, 3.83% H; found: 68.30% C, 3.74% H. ¹H NMR spectrum: 7.08 (dd, H-5, *J*(5, 6) = 8.6, *J*(5, 2) = 0.7), 7.84 (dd, H-6, *J*(6, 6) = 8.6, *J*(6, 2) = 2.1), 7.87 (dd, H-2, *J*(2, 6) = 2.1, *J*(2, 5) = 0.7), 4.03 (s, OCH₃). UV spectrum: λ_{\max} 304 nm (ϵ 272 m² mol⁻¹), 251 (1 280), 228 (4 070).

Photohydrolysis of IIa. 3,4-Dimethoxyacetophenone (*IIa*) (181 mg, 1.00 mmol) and potassium hydroxide (2.69 g, 0.048 mol) were irradiated for 6 h (25% conversion). TLC and HPLC analyses of the crude reaction mixture indicated the formation of a single photoproduct which was identified as 3-hydroxy-4-methoxyacetophenone (*Iib*) by comparison with an authentic sample. The yield of *Iib* was determined from quantitative HPLC analyses using benzene as internal standard.

Photocyanation of IIa. 3,4-Dimethoxyacetophenone (*IIa*) (180 mg, 1.00 mmol) and potassium cyanide (2.08 g, 0.032 mol) were irradiated for 6 h (30% conversion). After the usual workup, the crude photolyzate was quantitatively analyzed by means of GLC with the help of authentic samples of 3-cyano-4-methoxyacetophenone (*IIid*) and 4-cyano-3-methoxyacetophenone using tetradecane as internal standard.

Determination of Quantum Yields

Quantum yields of the disappearance of the aromatic substrates were calculated from the GLC determined time vs conversion data obtained during the preparative photolyses (Table I, entries 2, 3, 5, and 6). For this purpose we utilized the equation¹⁷ (*I*), where c_0 is the initial concentration of the starting compound (mol l⁻¹) and c_t is the actual concentration at the time t_r (s).

$$\Phi = \frac{c_0}{I_0 t_r} \ln (c_0/c_t) \quad (I)$$

The incident light intensity I_0 (mol quanta s⁻¹) was determined by ferrioxalate actinometry¹⁸. The TNN-15 lamp was left to burn for 10 min outside the preparative photoreactor charged with

the actinometric solution and was then introduced as quickly as possible. The estimated error in the determination of I_0 is approximately $\pm 30\%$ and is induced mainly by the short irradiation period (10 to 20 s). Quantum yields of the photohydrolysis and photocyanation of 1,2-dimethoxybenzene (*IV*) were determined by the same method at 2.5 mmol l^{-1} substrate concentration and 0.1 M-KOH or 0.1 M-KCN in 33% aqueous tert-butanol.

RESULTS AND DISCUSSION

3,4-Dimethoxybenzotrile (*Ia*) and 3,4-dimethoxyacetophenone (*IIa*) were photolyzed in the presence of either hydroxide or cyanide anion by monochromatic UV light (254 nm). The preparative yields from the photolyses are summarized in Table I. As can be seen from the distribution of the products there is a pronounced difference between the two nucleophiles.

When irradiated in dilute KOH solutions, both *Ia* and *IIa* gave a single photo-substitution product corresponding to the nucleophilic attack at the carbon atom C-3. The presence of the other isomer was unambiguously excluded by GLC, TLC and HPLC analyses of the reaction mixtures using authentic reference samples. The recovery of all low-molecular weight compounds in the case of the acetophenone *IIa* photohydrolysis is rather low (Table I, entry 5). Therefore, by irradiating the mixture of *Iib* (0.5 mmol l^{-1}) and *Iic* (0.5 mmol l^{-1}) under the same conditions as in the photolysis of *IIa* we have investigated the possibility of a preferential photodestruction of *Iic*. As a result, both isomers were found to disappear with about the same rate corresponding to approximately one tenth of the *IIa* disappearance. The low

TABLE I

Preparative photolyses of 3,4-dimethoxybenzotrile (*Ia*) and 3,4-dimethoxyacetophenone (*IIa*) in the presence of potassium hydroxide and potassium cyanide. Substrate concentration 2.5 mmol l^{-1} in 33% aqueous tert-butanol, excitation wavelength 254 nm

Exp.	Substrate	Nu ⁻	c_{Nu} mol l^{-1}	t_{irr} h	conversion %	Products (<i>I</i> or <i>II</i>), % ^a			
						<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
1	<i>Ia</i>	OH ⁻	0.18	2	5	64 ^b	0	--	--
2	<i>Ia</i>	OH ⁻	0.18	8	14	58 ^b	0	--	--
3	<i>Ia</i>	CN ⁻	0.08	9	10	--	--	24	49
4	<i>Ia</i>	CN ⁻	0.80	6	12	--	--	11	64
5	<i>IIa</i>	OH ⁻	0.12	6	25	18	0	--	--
6	<i>IIa</i>	CN ⁻	0.08	6	30	--	--	28	18
7	<i>IIa</i>	CN ⁻	0.80	3	25	--	--	31	22

^a Yields are related to the amount of the starting compound reacted; ^b 3,4-dimethoxybenzaldehyde (*V*, 10–12%) was also formed.

recovery of isolable products can be tentatively ascribed to the side reactions associated with the carbonyl group. Radical reactions of some methoxy-substituted acetophenones, initiated by the homolytic α -scission, were observed by Letsinger and coworkers¹⁹.

The same test of the relative photochemical stability with very similar results was performed also in the case of the two isomeric cyanomethoxyphenols *Ib* and *Ic*. Moreover, a comparison of entries 1 and 2 in Table I indicates that from the very beginning of the photolysis the *meta*-substitution product *Ib* is formed exclusively. In the former experiment the final conversion was as low as 5%, the starting compound still acting as a very efficient internal UV filter. Small amount of 3,4-dimethoxybenzaldehyde was also formed in the photohydrolysis of *Ia*. This can be explained by the experiments of Ferris and Antonucci²⁰ who described the conversion of hydroxy-substituted benzonitriles into the corresponding aldehydes by ultraviolet photolysis in alkaline aqueous solution. The reaction occurs as a photoreduction-hydrolysis sequence, starting from the hydroxybenzonitrile radical-anion generated by photoinduced electron transfer.

On the other hand, photoreactions of benzonitrile *Ia* as well as acetophenone *IIa* with the cyanide anion are non-selective, yielding both possible substitution products (Table I, entries 3, 4, 6, and 7). Besides, the distribution of the dicyanomethoxybenzenes *Id* and *Ie* resulting from the photocyanation of *Ia* depends on the nucleophile molar excess (n_r). At n_r 30 the ratio of isomers *Id*/*Ie* equals 1 : 2 while at n_r 300 it reaches the value of 1 : 6. The *para*-substitution product *Ie* dominates in each case, which is in fact a reversal of regioselectivity when compared with the photoreaction of *Ia* with hydroxide anion. It is worth mentioning that despite of the high alkalinity of the potassium cyanide solutions no photohydrolysis products were observed. Apparently the photochemical nucleophilic reactivity of CN^- is much greater than that of OH^- anion.

The striking difference in regioselectivity between the two nucleophiles is difficult to explain on the basis of the available experimental data. The overall photoreactivity of *Ia* and *IIa* is very low which from purely practical reasons makes impossible any steady-state kinetic measurements. Unfortunately, the same is true for the methods of fast spectroscopy because of the relatively large proportion of side reactions involved. It is nevertheless well possible to monitor the interactions between the nucleophilic anions and singlet excited substrates by means of the fluorescence quenching. It was found that the luminescence properties of the substrates (0.15 mmol l^{-1} in 50% aqueous methanol) are not affected by the presence of the hydroxide anion, up to 0.8M-KOH . On the contrary, cyanide anion strongly affects the luminescence of both compounds. The interaction between CN^- and the singlet excited states of acetophenone *IIa* is probably of complex nature since in some parts of the excitation spectrum the intensity is lowered and, at the same time, it is enhanced in other parts (see Fig. 1a).

The fluorescence excitation spectrum of benzonitrile *Ia* is also substantially changed upon the addition of KCN (see Fig. 1*b*). The decrease in the emission intensity is much more pronounced in the region near 254 nm, where $S_0 \rightarrow S_2$ excitation occurs, than in the part of the spectrum which corresponds to the $S_0 \rightarrow S_1$ excitation. The respective Stern–Volmer plots for the quenching of the S_1 and S_2 states of *Ia* are depicted in Fig. 2.

The dependence of the relative reciprocal fluorescence intensity upon the cyanide concentration is markedly non-linear at the 254 nm excitation wavelength which indicates possible involvement of at least two distinct quenching mechanisms; this

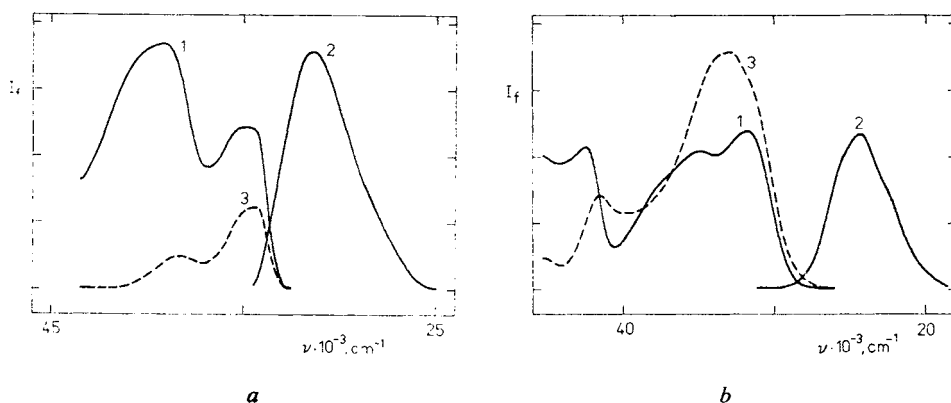


FIG. 1

Fluorescence spectrum of (a) *Ia* (0.15 mmol l⁻¹) and (b) *IIa* (0.18 mmol l⁻¹) in 50% aqueous methanol. 1 Excitation, 2 emission, 3 excitation spectrum at 0.8M-KCN

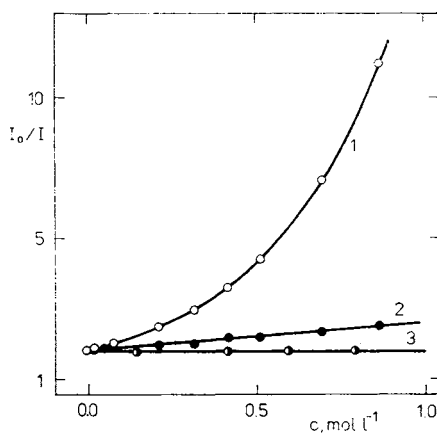


FIG. 2

Stern–Volmer plot for the quenching of *Ia* fluorescence (0.15 mmol l⁻¹ in 50% aqueous methanol), emission wavelength 308 nm. 1 Quenching by potassium cyanide, λ_{exc} 254 nm, 2 quenching by potassium cyanide, λ_{exc} 288 nm, 3 quenching by potassium hydroxide, λ_{exc} 254 nm

observation may be probably related to the concentration dependence of regioselectivity in the photocyanation of *Ia*. The results of the fluorescence quenching clearly indicate that the major difference between the hydroxide and cyanide anion lies in the multiplicity of the substrate excited state with which they interact. The photohydrolysis of both *Ia* and *IIa* occurs either with a direct involvement of the triplet excited states or, more likely, with the intermediacy of radical anions generated from the T_1 states. This hypothesis is strongly supported, at least in the case of *Ia*, by the radical anion-derived side products mentioned above. It can be concluded that the $-\text{CN}$ and $-\text{COCH}_3$ groups can not be classified unambiguously as *meta*-directing substituents. The question is what is their overall activation effect. In an attempt to describe it quantitatively we have calculated the quantum yields of photohydrolysis and photocyanation for the complete series of 3,4-dimethoxy-1-*R*-substituted benzene derivatives ($R = \text{H}, \text{CN}, \text{COCH}_3, \text{NO}_2$); the results are summarized in Table II.

It should be noted that the relevant photoreactions of *IV* ($R = \text{H}$) were first described by Den Heijer and coworkers²¹ but no quantum yields were given. As can be seen from the data collected in Table II, the quantum yields of photohydrolysis, relatively to 1,2-dimethoxybenzene as a reference substrate, are 1 : 2.5 : 5 : 580 and very similar relative reactivities were observed for the reaction with the cyanide anion (1 : 1.5 : 6 : 1000). The overall reactivity of the cyano and acetyl substituted dimethoxybenzene derivatives are thus about the same as that of the unsubstituted 1,2-dimethoxybenzene, while the quantum yields for 3,4-dimethoxy-1-nitrobenzene are at least by two orders of magnitude higher.

Summarizing the results, we have established that the orientation effects of the cyano as well as acetyl substituents, unlike in the case of $-\text{NO}_2$, depend on the nature of the inorganic nucleophile. Photoreactions with OH^- are selective leading exclusively to the *meta*-substituted products, while a lack of selectivity was observed in the

TABLE II

Quantum yields of photochemical reactions of 3,4-dimethoxy-1-*R*-substituted benzene derivatives with hydroxide or cyanide anion

R	$\phi \cdot 10^2$	
	OH^-	CN^-
H	0.02 ± 0.006	0.02 ± 0.006
CN	0.05 ± 0.015	0.03 ± 0.01
COCH_3	0.10 ± 0.03	0.12 ± 0.04
NO_2	11.6 ± 0.2 ^a	20.1 ± 0.2 ^b

^a In water, taken from ref. 22; ^b taken from ref. 8.

analogous photoreactions with the CN^- anion. A possible clue for an explanation of these differences is offered by the results of the fluorescence quenching study which has revealed that only the CN^- anion interacts with the singlet excited states of the aromatic substrates. The activation power of both $-\text{CN}$ and $-\text{COCH}_3$ substituents in nucleophilic aromatic photosubstitution is much lower in comparison with the nitro group.

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