REGIOSELECTIVITY OF NUCLEOPHILIC AROMATIC PHOTOSUBSTITUTION IN THE BIPHENYL SERIES. PHOTOHYDROLYSIS OF SOME DIMETHOXYNITROBIPHENYLS*

Jan URBAN, Petr KUZMIČ, David ŠAMAN and Milan SOUČEK

Institute of Organic Chemistry and Biochemistry,
*Czechoslovak Academy of Sciences, 166 10 Prague*

Anaerobic photolysis of dimethoxynitrobiphenyls *IIIa—VIa* in aqueous alkaline tert-butanol gave products of nucleophilic photosubstitution of methoxyl by hydroxide anion, while the dimethoxybiphenyls *Ia* and *IIa* were found unreactive. Regioselectivity of the reaction was examined in view of a possible "extended *meta* activation" by the nitro group. The most reactive substrate *IIIa* gives both C-3 and C-4 substitution products with an unsubstantial preference for the latter, which opposes the "extended *meta* selectivity" rule. All of the other compounds obey the rule, and 3,4-dimethoxy-3′-nitrobiphenyl (*IVa*) even displayed absolute selectivity by yielding C-3 substituted compound as the only product. 2,5-Dimethoxy substituted compounds underwent photosubstitution with much lower quantum yields than their 3,4-substituted counterparts, most probably due to some steric hindrance of conjugation. Similarly, 3-nitro-substituted biphenyls exhibited much lower overall reactivity than 4-nitro derivatives.

Structure–reactivity relationships in nucleophilic aromatic photosubstitution, and especially the substituent effects, have attracted much attention both of experimental photochemists[1] as well as theoretitians[2]. Among the most interesting general reactivity patterns found in this class of reactions there is a unique activating effect of the nitro substituent, which not only makes an aromatic system susceptible for the nucleophilic attack, but usually displays also significant selectivity directing properties. In most of the photosubstitution reactions of nitrobenzene derivatives bearing suitable leaving groups, the nitro substituent directs a nucleophile to the *meta* position[3].

An interesting photochemical behaviour was observed in the case of methoxynitronaphthalene derivatives[4]. For example, 1-methoxy-5-nitronaphthalene was found to be totally unreactive when photolyzed in the presence of hydroxide ion. On the other hand, 1-methoxy-6-nitronaphthalene underwent nucleophilic photosubstitution efficiently. An analogous pair of unreactive/reactive substrate is represented by 2-methoxy-6-nitro- and 2-methoxy-5-nitronaphthalenes, respectively. In these examples, however, the interpretation of regioselectivity and the assesment

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of possible substituent effect transmission are blurred by non-equivalence of the competing reaction centers. A decision could be made on the basis of the following experiments[4]: Photolysis of 2,3-dimethoxy-5-nitronaphthalene in aqueous alkaline solution gave 2-hydroxy-3-methoxy-5-nitronaphthalene, while the isomeric 6-nitro derivative underwent substitution at C-3 (see Scheme 1). This particular phenomenon was referred to as an "extended *meta* activation" effect of the nitro group, since — as in the benzene series — the reaction centre is separated from the activating substituent by an odd number of skeletal carbon atoms.
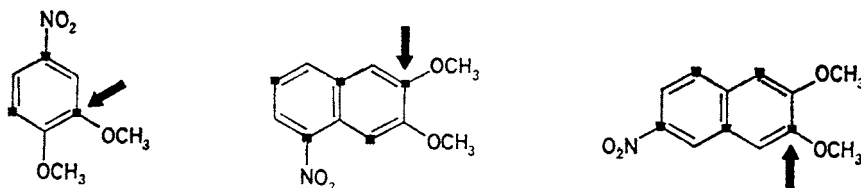
SCHEME 1

In Schemes 1 and 2, numbers indicate relative reactivities measured by quantum yield of hydrolysis product formation; arrows of different length express the observed regioselectivity, while the reaction centers predicted by the "extended *meta*" rule are indicated by full squares

In line with our ongoing studies in structure–reactivity relationships in aromatic nucleophilic photosubstitution, we were interested whether the same effect could be observed in case the two benzene rings were not fused. As for the methoxynitro-biphenyl derivatives bearing nitro group on one phenyl ring and the leaving methoxyl on the other one, there are no data in the literature with the exception of 4-methoxy--4'-nitrobiphenyl[5] which undergoes light induced methoxyl substitution by hydroxide anion. An explanation is offered in terms of the transition state structure represented by the formula *A*. Noteworthy, the foregoing example does not follow the "extended

A
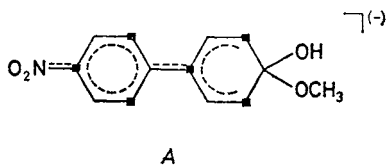
meta activation" rule but, again, the interpretation is not straightforward because of non-equivalence of the competing positions. Therefore, we decided to examine the photochemical reactivity of suitable dimethoxy-substituted biphenyls which would allow an unambiguous assesment of the possibility for any "extended *meta* activation".

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. High-resolution mass spectra were measured with an AEI MS-902 instrument, electron energy 70 eV, source temperature 150—250°C. UV spectra were recorded on a Specord UV/VIS (Zeiss, Jena) in methanol; positions of the absorption maxima are given in nm, values in parentheses are the corresponding molar absorption coefficients in $m^2 mol^{-1}$. UV spectral measurements for the determination of quantum yields were made with a Varian Cary 219 spectrophotometer, spectral band-width 1·5 nm. ^{1}H NMR spectra were measured on a Varian XL-200 spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. Chemical shifts (in ppm) and the interaction constants (in parentheses, Hz) were determined by first-order analysis. Structures of the individual compounds were established by comparison of the experimental shifts, as well as interaction constants, with the values predicted on the basis of empirical additive rules[6]. The ratio of regioisomers *IIIb/IIIc* and *VIb/VIc* was determined from integrated peak areas. The structures of phenol derivatives *Ib— VIb* and *Ic— VIc* were resolved after *in situ* derivatization of these compounds by trichloroacetyl isocyanate (TAI)[7,8]. The observed changes in chemical shifts upon acylation of a phenolic hydroxyl were 0·3—0·4 ppm for *ortho/para* and 0·1—0·2 ppm for *meta* hydrogen atoms, in accordance with the published data.

Preparative chromatography was run on a 3 × 30 cm column of 30—60 μm gel deactivated with 15% of water, elution with light petroleum–diethyl ether (10 : 1). Fractions were analyzed by thin-layer chromatography on silica gel (Woelm G-DC), elution with light petroleum–diethyl ether (10 : 1) or light petroleum–toluene–acetone (5 : 5 : 1); spots were visualized by spraying with 5% solution of cerium(IV) sulphate in $2M-H_2SO_4$ and pyrolysis. Preparative thin-layer chromatography was performed on 20 × 20 × 0·1 cm plates of silica gel (Merck GF-254, type 60), elution with light petroleum–toluene–acetone (3 : 3 : 1). The developed bands were visualized in UV light and were extracted with chloroform. High-performance liquid chromatography was performed with a 25 × 0·4 cm column of 5 μm modified silica gel Separon SI C-18, elution with 70% aqueous methanol, UV detection at 254 or 365 nm.

Tert-butanol was filtered through charcoal and distilled. Deionized water was distilled from potassium permanganate. Benzene was distilled from sodium and acetonitrile was distilled from phosphorus pentoxide. Traces of oxygen were removed from the argon in an absorption apparatus[9] filled with a deoxygenation solution according to Meites[10]. 3- And 4-nitrobenzenediazonium tetrafluoroborates[11], 1-iodo-3,4-dimethoxybenzene[12], and 1-iodo-2,5-dimethoxybenzene[13] were prepared according to previously described methods. 2,4-Hexadienoic acid was recrystallized three times from water, m.p. 133—134°C, ref.[14] m.p. 133°C.

Preparation of *Ia* and *IIa*

1-Iodo-3,4- or 1-iodo-2,5-dimethoxybenzene (1·00 g; 3·8 mmol) was dissolved in benzene (400 ml). The solution was deoxygenated with a stream of argon (15 min) and irradiated in a water-cooled preparative immersion-well photoreactor (Fritz, Hofheim, F.R.G.). A medium pressure mercury lamp (RVK-125, Tesla) in a Pyrex sleeve (2 mm thickness) was used as the light source. Powdered sodium thiosulphate in small portions was being added during the irradiation to remove the iodine formed. After 8 h of irradiation, solvent was removed *in vacuo* and products were isolated by column chromatography on silica gel.

3,4-*Dimethoxybiphenyl* (Ia), m.p. 69—70°C (isooctane, ref.[15] m.p. 70·5—71·5°C), yield 62%. UV spectrum: 265 (1 550). ^{1}H NMR spectrum: see Table I.

2,5-*Dimethoxybiphenyl* (IIa), oil (ref.[16] oil), yield 65%. UV spectrum: 304 (465), 254 (630), 219 (1 890). ^{1}H NMR spectrum: see Table II.

TABLE I

Chemical shifts in ^{1}H NMR spectra of 3,4-dimethoxysubstituted biphenyls and of their photolysis products

Proton[a]	Ia	Ib[b]	Ic[b]	IIIa	IIIb[b]	IIIc[b]	IVa	IVb
H-2	7·11 d	7·08 dd	7·20 d	7·13 d	6·96 d	7·03 d	7·12 d	7·09 d
H-5	6·95 d	6·99 dd	6·92 d	6·99 d	7·23 d	7·11 d	6·99 d	7·02 d
H-6	7·15 dd	7·11 dd	7·09 dd	7·02 dd	7·15 dd	7·17 dd	7·20 dd	7·15 dd
H-2′	—[c]	—[c]	—[c]	7·70 m	7·68 m	7·68 m	8·41 dt	8·38 t
H-3′	—[c]	—[c]	—[c]	8·28 m	8·27 m	8·27 m	—	—
H-4′	—[c]	—[c]	—[c]	—	—	—	8·17 ddd	8·14 ddd
H-5′	—[c]	—[c]	—[c]	8·28 m	8·27 m	8·27 m	7·59 ddd	7·57 ddd
H-6′	—[c]	—[c]	—[c]	7·70 m	7·68 m	7·68 m	7·89 ddd	7·87 ddd
OCH$_3$	3·93 s	3·92 s	3·95 s	3·95 s	3·97 s	3·99 s	3·92 s	3·99 s
OCH$_3$	3·95 s	—	—	3·98 s	—	—	3·95 s	—
OH	—	5·64 bs	5·66 bs	—	5·72 bs	5·78 bs	—	5·75 bs

[a] Coupling constants for $Ia-Ic$: $J(2, 6) = 2·1$, $J(5, 6) = 8·2$; for $IIIa-IIIc$: $J(2, 6) = 2·2$, $J(5, 6) = 8·4$, $J(2′, 3′) = 8·9$, $J(5′, 6′) = 8·9$; for IVa, IVb: $J(2, 6) = 2·0$, $J(5, 6) = 8·2$, $J(2′, 4′) = 2·2$, $J(2′, 5′) = 0·3$, $J(2′, 6′) = 1·9$, $J(4′, 5′) = 8·3$, $J(4′, 6′) = 1·1$, $J(5′, 6′) = 7·8$. [b] From the spectrum of a mixture of regioisomers (see Experimental). [c] Signal is in the range 7·26—7·60 ppm.

TABLE II

Chemical shifts in ^{1}H NMR spectra of 2,5-dimethoxysubstituted biphenyls and of their photolysis products

Proton[a]	IIa	Va	Vb	Vc	VIa	VIb[b]	VIc[b]
H-3	6·91 dd	6·92 m	6·87 m	6·88 m	6·94 m	6·88 m	6·88 m
H-4	6·84 dd	6·92 m	6·87 m	6·88 m	6·94 m	6·88 m	6·88 m
H-6	6·91 dd	6·95 m	6·87 m	6·85 m	6·94 m	6·88 m	6·88 m
H-2′	—[c]	7·70 m	7·69 m	7·72 m	8·42 ddd	8·44 ddd	8·41 ddd
H-3′	—[c]	8·26 m	8·23 m	8·31 m	—	—	—
H-4′	—[c]	—	—	—	8·18 ddd	8·22 ddd	8·18 ddd
H-5′	—[c]	8·26 m	8·23 m	8·31 m	7·56 ddd	7·62 ddd	7·56 ddd
H-6′	—[c]	7·70 m	7·67 m	7·72 m	7·86 ddd	7·89 ddd	7·85 ddd
OCH$_3$	3·73 s	3·78 s	3·77 s	3·81 s	3·78 s	3·82 s	3·78 s
OCH$_3$	3·79 s	3·82 s	—	—	3·82 s	—	—
OH	—	—	4·70 bs	4·70 bs	—	4·70 bs	4·70 bs

[a] Coupling constants for IIa: $J(3, 4) = 9·0$, $J(3, 6) = 0·8$, $J(4, 6) = 2·7$; for $Va-Vc$: $J(4, 6) = 2·4$ $J(2′, 3′) = 9·0$; for $VIa-VIc$: $J(2′, 4′) = 2·2$, $J(2′, 5′) = 0·4$, $J(2′, 6′) = 1·7$, $J(4′, 5′) = 8·2$, $J(4′, 6′) = 1·1$, $J(5′, 6′) = 7·8$. [b] From the spectrum of a mixture or regioisomers (see Experimental). [c] Signal is in the range 7·26—7·56 ppm.

Preparation of *IIIa* and *IVa*

The solution of 3- or 4-nitrobenzenediazonium tetrafluoroborate (1·00 g; 4·22 mmol) and di-benzo-18-crown-6 (120 mg; 0·33 mmol) in 1,2-dimethoxybenzene (10·9 g; 78·1 mmol) was stirred under argon with the exclusion of light (10 min). Potassium acetate (0·84 g; 8·56 mmol) was added in one portion and stirring was continued for additional 60 min at room temperature. The mixture was filtered and the filter cake was washed with benzene. The filtrate was washed with brine and the aqueous layer was back-extracted with benzene. The combined organic layers were dried with magnesium sulphate and the solvent was removed by vacuum evaporation. The unreacted 1,2-dimethoxybenzene was distilled off at 50 Pa and 120°C bath temperature and the desired product was isolated from the residue by preparative column chromatography.

3,4-*Dimethoxy-4'-nitrobiphenyl* (IIIa), m.p. 131—132°C (benzene, ref.[15] m.p. 132·5—133·5°C), yield 37%. UV spectrum: 349 (1 260), 267 sh (820), 238 (1 090). ^{1}H NMR spectrum: see Table I.

3,4-*Dimethoxy-3'-nitrobiphenyl* (IVa), m.p. 92—93·5°C (hexane–ether), yield 37%. For $C_{14}H_{13}NO_4$ (259·3) calculated: 64·85% C, 5·06% H, 5·40% N; found: 64·96% C, 5·05% H, 5·44% N. Mass spectrum: calculated 259·0844, found 259·0837. UV spectrum: 333 (160), 294 sh (780), 267 (1 460), 229 sh (1 420). ^{1}H NMR spectrum: see Table I.

Preparation of *Va* and *VIa*

The solution of 1,4-dimethoxybenzene (10·0 g; 72·4 mmol), 3- or 4-nitrobenzenediazonium tetrafluoroborate (1·00 g; 4·22 mmol) and dibenzo-18-crown-6 (120 mg; 0·33 mmol) in acetonitrile (20 ml) was stirred under argon with the exclusion of light for 10 min. Potassium acetate (0·84 g; 8·56 mmol) was added in one portion and stirring was continued for 60 min. The same work-up as described above gave the desired products.

2,5-*Dimethoxy-4'-nitrobiphenyl* (Va), m.p. 114—115°C (hexane, ref.[17] m.p. 116·6°C), yield 48%. UV spectrum: 344 (540), 301 sh (770), 256 (1 020). ^{1}H NMR spectrum: see Table II.

2,5-*Dimethoxy-3'-nitrobiphenyl* (VIa), m.p. 80—81°C (pentane–ether), yield 55%. For $C_{14}H_{13}$.NO_4 (259·3) calculated: 64·85% C, 5·06% H, 5·40% N; found: 65·03% C, 5·06% H, 5·40% N. Mass spectrum: calculated 259·0844, found 259·0852. UV spectrum: 307 (680), 254 (1 500), 219 (2 820). ^{1}H NMR spectrum: see Table II.

Demethylation of *Ia*

A mixture of sodium iodide (160 mg; 1·07 mmol), 3,4-dimethoxybiphenyl (28 mg; 1·06 mmol), and chloroform (500 μl) was stirred under argon and trimethylsilyl chloride (120 mg; 1·1 mmol) was added in one portion. After 16 h of stirring, methanol (8 ml) and saturated aqueous sodium chloride solution (20 ml) were added. The mixture was extracted with ether (3 × 20 ml). Ethereal extracts were dried with magnesium sulphate and the solvent was evaporated *in vacuo*. The residue was dissolved in benzene (30 ml) and the solution was extracted with 2м-NaOH (3 × 10 ml). The alkaline extracts were acidified with concentrated hydrochloric acid and were extracted with benzene. Drying with magnesium sulphate and evaporation *in vacuo* gave a mixture of 3-hydroxy-4-methoxybiphenyl (*Ic*) and 4-hydroxy-3-methoxybiphenyl (*Ib*) (13 mg, 6%). The mixture was purified by preparative TLC and showed a single spot in TLC under various conditions as well as a single peak (min. 99% absorbance at 254 nm) in HPLC analysis. Mass spectrum of the mixture: for $C_{13}H_{12}O_2$ calculated 200·0835, found 200·0837. ^{1}H NMR spectrum: see Table I.

Preparative Photolyses

The appropriate biphenyl derivative (30 to 70 mg) was dissolved in tert-butanol (200 ml) and the solution was mixed with 0·2M-NaOH (200 ml). The mixture was deoxygenated with a stream of argon (20 min) and irradiated in a preparative water-cooled immersion-well photoreactor (Fritz, Hofheim, F.R.G.). The reaction conditions are indicated in Table I. The reaction mixture was neutralized with 2M-HCl and was saturated with sodium chloride. The organic layer was separated, diluted with chloroform (200 ml), and dried with magnesium sulphate. Solvents were evaporated *in vacuo* and products were isolated from the crude photolysate by preparative column chromatography in combination with preparative TLC.

Ia: HPLC analysis using a mixture of *Ib* and *Ic* as reference sample, revealed that these compounds were not present in the photolysate which was not further investigated.

IIa: Only the starting compound could be detected by HPLC of the photolysate.

IIIa: Column chromatography followed by preparative TLC gave yellow crystals (for yield see Table III) which showed a single spot in TLC as well as a single peak in HPLC (min. 99% absorbance at 365 nm). This fraction was shown to be a mixture of 4-hydroxy-3-methoxy-4′--nitrobiphenyl (*IIIb*) and 3-hydroxy-4-methoxy-4′-nitrobiphenyl (*IIIc*) by means of spectroscopic methods. Mass spectrum: for $C_{13}H_{11}NO_4$ calculated 245·0688, found 245·0695. ^1H NMR spectrum: see Table I.

IVa: Besides of the unreacted starting material, 4-hydroxy-3-methoxy-3′-nitrobiphenyl (*IVb*) was isolated as the only product, m.p. 98—100°C (hexane–ether). Mass spectrum: for $C_{13}H_{11}NO_4$ calculated 245·0688, found 245·0684. ^1H NMR spectrum: see Table I.

Va: Column chromatography followed by repeated preparative TLC gave *Vb* and *Vc*. 5-Hydroxy-2-methoxy-4′-nitrobiphenyl (*Vb*), m.p. 132—133°C (hexane–ether). Mass spectrum: for $C_{13}H_{11}NO_4$ calculated 245·0688, found 245·0686. ^1H NMR spectrum: see Table II. 2-Hydroxy--5-methoxy-4′-nitrobiphenyl (*Vc*), m.p. 154—156°C (hexane–ether). Mass spectrum: for $C_{13}.H_{11}NO_4$ calculated 245·0688, found 245·0686. ^1H NMR spectrum: see Table II.

VIa: Column chromatography followed by preparative TLC gave yellow crystals which showed a single spot in TLC as well as a single peak in HPLC (min. 99% absorbance at 254 nm). This fraction was shown to be a mixture of 5-hydroxy-2-methoxy-3′-nitrobiphenyl (*VIb*) and 2-hydroxy-5-methoxy-3′-nitrobiphenyl (*VIc*) by means of spectroscopic methods. All attempts to separate the isomers failed. Mass spectrum: for $C_{13}H_{11}NO_4$ calculated 245·0688, found 245·0694. ^1H NMR spectrum: see Table II.

Determination of Quantum Yields

A solution of biphenyl derivative of the initial concentration c_0 ranging from 0·3 to 0·8 mmol l^{-1} in 50% (v/v) aqueous tert-butanol (0·1M-NaOH) was irradiated in the preparative photoreactor as described above with a low-pressure mercury lamp Hanau TNN-15. Total irradiation time t (5 min to 5 h) was chosen so as to keep the conversion below 20%. The final concentration c_t of the starting compound was determined by means of HPLC analysis. UV absorption spectrum of the reaction mixture was measured before as well as after the photolysis and the apparent molar absorption coefficient of the sum of photochemical products (a_P) was calculated from Eq. (*1*), where A_t is the final absorbance at the excitation wavelength (254 nm) and a_S is the known absorption coefficient of the starting compound at this wavelength.

$$A_t = c_t a_S + (c_0 - c_t) a_P \qquad (1)$$

The incident light intensity I_0 (mol quanta s^{-1}) was determined by chemical actinometry according to Pavlíčková et al.[18]. The quantum yields were calculated[19] according to Eq. (2), where x is the ratio of molar absorption coefficients a_P/a_S.

$$\Phi_r = [c_t(1 - x) + xc_0 \ln (c_0/c_t)]/I_0 t \qquad (2)$$

RESULTS AND DISCUSSION

As to be able to asses the overall activation effect of the nitro group, we have exploited the photolysis of dimethoxybiphenyl derivatives *Ia* and *IIa* as reference compounds (the results of all preparative photolyses are summarized in Table III). Although *Ia* yielded a complex mixture by extensive irradiation, none of the expected demethylation products were present in the photolyzate. The estimated quantum yield of *Ia* photodestruction was as low as 0·0001. Similar results were obtained with *IIa*, which showed complete photochemical stability under the given conditions.

OR¹ as LaTeX:

OR^1 ... the figure:
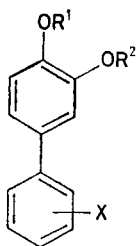
I, X = H
II, X = 4'-NO$_2$
IV, X = 3'-NO$_2$
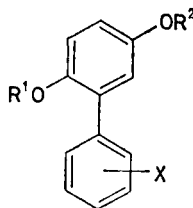
II, X = H
V, X = 4'-NO$_2$
VI, X = 3'-NO$_2$

In formulae I–VI : a, R¹= R²= CH$_3$; b, R¹= H , R²= CH$_3$;
c, R¹= CH$_3$, R²= H

The greatest overall photochemical reactivity, as measured by the quantum yield, was shown by 3,4-dimethoxy-4'-nitrobiphenyl (*IIIa*). For this substrate, the "extended *meta* selectivity" rule predicts a nucleophilic photosubstitution reaction to occur on the atom C-3, yielding 3-hydroxy-4-methoxy-4'-nitrobiphenyl (*IIIc*). Nevertheless, we have observed the formation of both possible photoproducts *IIIb* and *IIIc* in the ratio 5 : 4. This means that the observed regioselectivity, if any, operates against the rule. The results of the 3,4-dimethoxy-3'-nitrobiphenyl (*IVa*) photolysis are quite different in two important aspects. Firstly, on switching from C-4' to C-3' nitro--substituted derivative the reaction quantum yield drops by two orders of magnitude. Secondly, the regioselectivity in this case strictly obeys the "extended *meta*" rule, because the predicted 4-hydroxy-3-methoxy-3'-nitrobiphenyl (*IVb*) is the only detectable photoproduct.

In comparison with their 3,4-dimethoxy-substituted counterparts, 2,5-dimethoxy-biphenyls *Va* and *VIa* showed a decrease of the overall photochemical reactivity, quite similar to that which was observed on going from C-4′ to C-3′ nitro substitution. Although the quantum yield of 2,5-dimethoxy-4′-nitrobiphenyl (*Va*) photohydrolysis is somewhat higher than that of *IVa*, it is still about thirty times lower when compared with *IIIa*. On the basis of the results mentioned above, one can assume that in 2,5-dimethoxy-3′-nitrobiphenyl (*VIa*) both the structural factors inducing low reactivity should combine. As can be seen from the data in Table III, this particular substrate, indeed, has an extremely low photohydrolysis quantum yield.

In the case of both *Va* and *VIa*, the regioselectivity is 7 : 4 and 4 : 1, respectively, in favor of the regioisomer predicted by the "extended *meta* selectivity" rule. We should mention that the least reactive substrate, *VIa*, yielded a significant amount of photolysis by-products, because the sum of *VIb* and *VIc* yields was only 30% (see Table III). The question arises, therefore, whether the regioisomer ratio observed in this case corresponds to the true reaction selectivity. Therefore, we checked the relative photostability of *VIb* and *VIc* by irradiating a mixture of the two compounds in a small-scale experiment. As a result, the relative abundance of *VIb* and *VIc* did not change. Apart from *VIa*, other compounds gave mass balances satisfactory enough (*IIIa* 100%, *IVa* 95%, *Va* 83%) to consider the corresponding photolysis product ratios sufficiently reliable.

TABLE III

Preparative photolyses of compounds *Ia—VIa* (50% aqueous tert-butanol, 0·1M-NaOH, argon atmosphere)

Compound	Light source[a]	Time h : min	Concentration mmol l^{-1}	Conversion %	Products[b]	Quantum yield
Ia	A	8 : 00	0·790	25	0·0[c]	0·0
Ia	A	31 : 40	0·695	60	0·0[c]	0·0
IIa	A	16 : 00	8·41[d]	0	0·0[c]	0·0
IIIa	B	0 : 20	0·587	80	56% *IIIb*, 44% *IIIc*	0·23[e]
IVa	A	28 : 15	0·639	90	96% *IVb*	0·0023
Va	B	21 : 00	0·462	80	53% *Vb*, 30% *Vc*	0·0071[e]
VIa	A	59 : 30	0·338	75	6% *VIb*, 24% *VIc*	0·0002[e]

[a] A — Low pressure mercury lamp Hanau TNN-15, quartz filter; B — medium pressure mercury lamp Tesla RVK-125, Pyrex filter. [b] Yields are based on converted starting material. [c] The expected products were not found in the reaction mixture. [d] Reaction volume 4 ml. [e] Sum of quantum yields for the formation of both products.

This allows us to discuss the summarized results. As can be seen from Scheme 2, the presence of the nitro substituent is essential for the reaction to occur at all, since the compounds not bearing it do not undergo photosubstitution. Besides, when attached to C-4′, the nitro group activates the adjacent phenyl ring much more than in C-3′ position. This observation can be most probably ascribed to some electronic effects — mainly mesomeric in nature (supposing that this classical notion can be applied to an open-shell electronic state). On the other hand, the explanation of relative reactivities of 3,4- vs 2,5-dimethoxybiphenyls is straightforward: The low reactivity of the latter substrates can be viewed as a result of steric factors. It seems that planarity of a key reactive intermediate (excited state, radical-ion) is essential for the above-mentioned electronic factors to be operative, in analogy with sterically induced loss of conjugation known from ground-state chemistry. The influence of ortho-substituents on the excited-state electronic structure of biphenyls, as reflected by pronounced changes in their electronic absorption spectra, is discussed in detail by Suzuki[20].
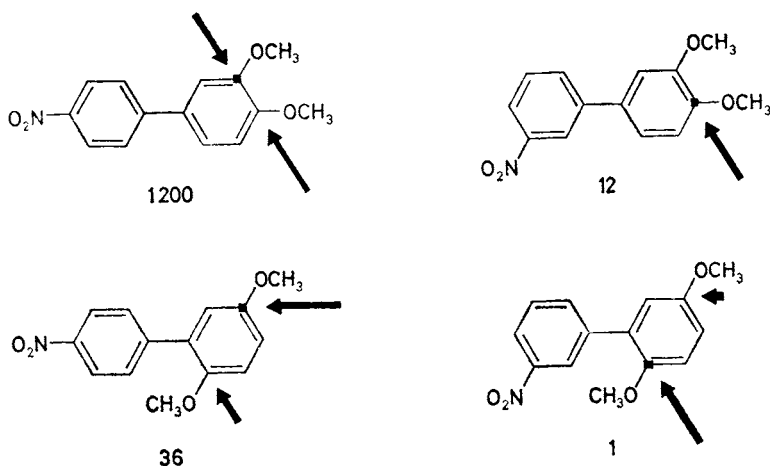
SCHEME 2

In our opinion, in a discussion of regioselectivity trends also indicated in Scheme 2 we can concentrate on electronic factors exclusively, because in all compounds the competing reaction centers are approximately equally achievable for a small nucleophilic anion. Unfortunately, as was indicated in the preceding paragraph, we can only speculate about the nature of these factors, which enable the activation effect of the nitro group not only to be transferred through the phenyl ring, but also to be transferred selectively. Let us only to note that, apart from any "extended meta activation", some intrinsic reactivity seems to belong to C-4, in analogy with the

excess "α-reactivity" observed in the naphthalene series[1]. Thus the formation of a single photosubstitution product from 3'-nitro derivative *IVa* can be interpreted as a combined synergistic effect of both "extended *meta* activation" and "α-reactivity", while the unselective photoreaction of *IIIa* represents a case in which the two factors operate in a mutually opposing fashion.

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