

PHOTOCYANATION OF 3,4-DIMETHOXY-1-NITROBENZENE. A QUANTITATIVE STUDY

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UV photolysis (365 nm) of 3,4-dimethoxy-1-nitrobenzene in the presence of potassium cyanide leading to 3-cyano-4-methoxy-1-nitrobenzene was subjected to a quantitative photokinetic study. The reaction exhibits a second order kinetics with respect to the nucleophile and is effectively quenched by molecular oxygen as well as 2,4-hexadienoic acid. The excited triplet lifetime of 0.9 microseconds was determined on the basis of the dependence of quantum yield on the nucleophile and quencher concentrations in 50% aqueous tert-butanol. The quantum yield of intersystem crossing is at least 0.38 in the same solvent; bimolecular rate constant for the interaction of triplet 3,4-dimethoxy-1-nitrobenzene with cyanide anion has the value of $5.6 \cdot 10^8 \text{ l. mol}^{-1} \text{ s}^{-1}$, which is approximately one half of the rate constant for diffusion controlled quenching. Quantum yield of the reaction is strongly dependent on the water content in mixtures with tert-butanol and increases from 0.04 in water to 0.68 in 88% tert-butanol.

Several decades ago nucleophilic aromatic photosubstitution (S_NAr^*) was discovered in two classes of aromatic derivatives, namely ethers and esters of nitrophenols. Among the two classes of compounds, nitrophenyl ethers have been attracting attention of photochemists ever since the discovery of S_NAr^* reactions (for review see refs¹⁻³). Substantial effort was devoted to the investigation of photokinetic behaviour of these substrates.

From the kinetic point of view, several nucleophilic photosubstitution reactions of nitrophenyl ethers investigated so far exhibit similar features. For example, there is a linear dependence of the reciprocal quantum yield on the reciprocal nucleophile concentration as well as a triplet quencher concentration. In this manner occurs the photohydrolysis of 3,5-dinitroanisole in alkaline media⁴. The proposed reaction mechanism is denoted as S_N2-3Ar^* to express the fact that it includes a bimolecular step with the involvement of the triplet excited substrate. For the sake of completeness it should be added that there are also other mechanistic types of S_NAr^* reactions, as for example the photocyanation of 2-nitrofurane leading to 2-cyanofurane⁵ whose quantum yield is independent on the nucleophile concentration. Such reaction is denoted as S_N1-Ar^* , since it involves a monomolecular heterolytic expulsion of the leaving group.

3,4-Dimethoxy-1-nitrobenzene is an interesting substrate of S_NAr^* reactions not only from the point of view of possible applications for photoaffinity labeling of biomolecules⁶ but also theoretically, with regard to the high regioselectivity generally observed in this class of reactions. On the example of this compound a striking difference in reactivity between ground and excited states can also be demonstrated; heating the solution of 3,4-dimethoxy-1-nitrobenzene in aqueous alkaline hydroxide leads to the formation of 2-methoxy-4-nitrophenolate anion by nucleophilic substitution. On the other hand, by UV photolysis of 3,4-dimethoxy-1-nitrobenzene under otherwise identical conditions the isomeric 2-methoxy-5-nitrophenolate can be obtained¹. The title molecule is a particularly interesting substrate for a quantitative mechanistic study also from the point of view of substitution effects on S_NAr^* reaction mechanisms since in its structure two different subunits could be discerned, *i.e.* of 3-nitroanisole – a classical substrate of $S_N2-^3Ar^*$ reactions¹ – and of 1,2-dimethoxybenzene which undergoes monomolecular photoionization/substitution reactions⁷ of the type $S_{R+N}1-Ar^*$.

Some of the nucleophilic photosubstitution reactions of nitrophenyl ethers were studied and their reaction mechanisms are sufficiently known⁴; the reverse is true for 3,4-dimethoxy-1-nitrobenzene, where kinetic data for the determination of excited state multiplicity and reaction molecularity are still missing. The photochemical studies concerning substitution reactions of 3,4-dimethoxy-1-nitrobenzene with inorganic nucleophiles (hydroxide⁸, methoxide⁸ and cyanide⁹ anion) as well as aliphatic amines³ were confined to the determination of quantum yields only.

Solvent effect is one of the most important factors influencing overall reactivity in nucleophilic photosubstitution reactions. For example, in the case of the $S_{R+N}1-Ar^*$ mechanism⁷ there is a striking increase of the reaction quantum yield with the increasing solvent polarity. As for the reactions of the $S_N2-^3Ar^*$ type, solvent effect was only scarcely investigated^{4,8}.

It is the aim of the present study to describe the photokinetic behaviour of the system 3,4-dimethoxy-1-nitrobenzene – potassium cyanide in mixed solvents, *i.e.* to determine *a*) multiplicity of the reactive excited state as well as the excited state lifetime, *b*) molecularity of the rate determining step and *c*) to investigate more deeply the effect of solvent mixture composition on reaction quantum yields.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. UV spectra were recorded on a Cary 219 spectrophotometer (spectral bandwidth 1.5 nm); for the determination of quantum yields the optical densities were read with an accuracy of ± 0.0002 absorbance units.

3,4-Dimethoxy-1-nitrobenzene was prepared by a standard procedure¹⁰ and was recrystallized twice from water, m.p. 94°C (lit.¹⁰ m.p. 93–94°C). Tert-butanol and water were distilled prior to use. Potassium cyanide was prepared by pouring 50% molar excess of liquid hydrogen cyanide

into an icecold solution of potassium hydroxide in methanol; the product was precipitated by ether, filtered off, washed subsequently with methanol and ether, dried *in vacuo* and stored under argon. Traces of oxygen were removed from argon gas in an absorber according to Tenygl¹¹ filled with the absorption solution devised by Meites¹². 2,4-Hexadienoic acid was three times recrystallized from water, m.p. 133–134°C (lit.¹³ m.p. 133°C).

Preparative Photolysis of 3,4-Dimethoxy-1-nitrobenzene (I)

3,4-Dimethoxy-1-nitrobenzene (I) (500 mg, 2.73 mmol) and potassium cyanide (2.00 g) were dissolved in the mixture of water and tert-butanol (400 ml, 3 : 1 v/v). The solution was irradiated with a medium-pressure mercury lamp RVK-125 (Tesla) at 18°C. The optical filtration system consisted of Pyrex glass filter (2 mm thickness) and a solution of 1,3-dimethyl-4,7-diaza-1,3-cycloheptadien perchlorate¹⁴ (0.40 g l⁻¹ in water, 5 mm thickness). After 70 min of irradiation the precipitated yellow crystals were collected, washed with water and recrystallized from light petroleum-ether yielding 210 mg (1.12 mmol) of 3-cyano-4-methoxy-1-nitrobenzene (II), m.p. 125–126°C (lit.¹⁵ m.p. 127.5–128°C). The remaining part of the reaction mixture was analyzed by thin-layer chromatography on silica gel (Woelm G-DC), elution with benzene-hexane-acetone 10 : 10 : 1. By comparison with authentic samples the photoproduct II, starting compound I and a trace amount of 2-methoxy-5-nitrophenol (III) besides of some highly polar unidentified by-products were detected. Column chromatography on silica gel gave 150 mg (0.82 mmol) of I and 99 mg (0.56 mmol) of II, yield 88% based on the amount of I reacted.

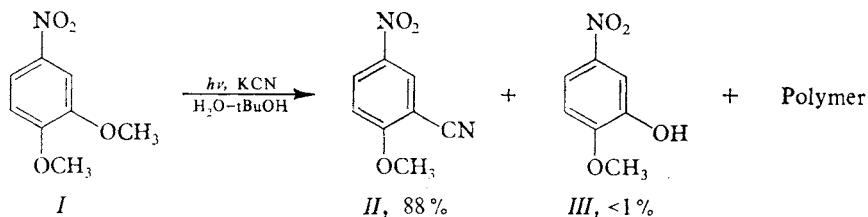
Determination of Quantum Yields

Stock solutions of the substrate and triplet quencher were prepared by dissolving 3,4-dimethoxy-1-nitrobenzene (46.4 mg, 0.254 mmol) in methanol (10 ml) and 2,4-hexadienoic acid (224 mg, 2.00 mmol) in methanol (10 ml). Stock solutions of the nucleophile were prepared by dissolving potassium cyanide (961 mg, 14.7 mmol) in water (10 ml, solution A) and by the dilution of solution A with water (1 : 10, solution B). Proper amounts of stock solutions (15.0 µl substrate, 10.0–33.0 µl solution A or 5.0–50.0 µl solution B, 10.0–70.0 µl quencher) were injected into a quartz cuvette containing 3.00 ml of the solvent and the sample was bubbled with argon (saturated with vapours of the solvent) for 15 min; each sample was irradiated with UV light of the wavelength 365 ± 10 nm while the continuous stream of argon was introduced. An HBO 200 (Osram) high-pressure mercury lamp in connection with an Applied Photophysics M-300 high intensity monochromator (reciprocal dispersion 4 nm mm⁻¹) was used as the light source. At regular time intervals (10 s) the absorbance at 340 nm was determined (total irradiation time 60 s); prior to and after each run the absorbance at 365 nm was also determined. Absorption data were evaluated by numerical integration of the photokinetic equation¹⁶. Final conversion did not exceed 20%. The incident light intensity was measured by a chemical actinometer based on the photohydrolysis of 3,4-dimethoxy-1-nitrobenzene described elsewhere¹⁶; typically we found $3.0 \cdot 10^{-14}$ mol quanta s⁻¹ m⁻².

RESULTS AND DISCUSSION

Photolysis of 3,4-dimethoxy-1-nitrobenzene in aqueous tert-butanol in the presence of potassium cyanide is accompanied by spectral changes shown in Fig. 1. It is apparent that the reaction exhibits a simple, well-defined course up to the total conversion of the starting compound since the isosbestic point at 319 nm is maintained during the whole irradiation period. Indeed, the preparative experiment

gave *II* as a major product (88% isolated yield), trace amount of the phenol *III* and some highly polar polymers (Scheme 1).



SCHEME 1

However, for the purpose of determining the dependence of the reaction quantum yield on various experimental conditions we consider a single photoproduct to which we ascribe the electronic absorption spectrum of the reaction mixture at total conversion (Fig. 1). Thus, kinetically the photocyanation of *I* can be considered as a simple irreversible photoreaction of the type $S \rightarrow P$, where *S* denotes the starting compound and *P* is the photoproduct. As follows from Figure 1, analyses of the reaction mixture can easily be achieved by means of the UV/VIS spectrometry. The molar absorption coefficients of *S* and *P* at the excitation wavelength are 505 and $64 \text{ m}^2 \text{ mol}^{-1}$, respectively, while at the arbitrarily chosen analytical wavelength (340 nm, corresponding to the absorption maximum of *S*) they have the value of 765 and $196 \text{ m}^2 \text{ mol}^{-1}$. Using these values and recently described methodology¹⁶ we were able to determine quantum yields directly from the spectral data. By this method we examined the dependence of quantum yield of photocyanation on the concentration of cyanide

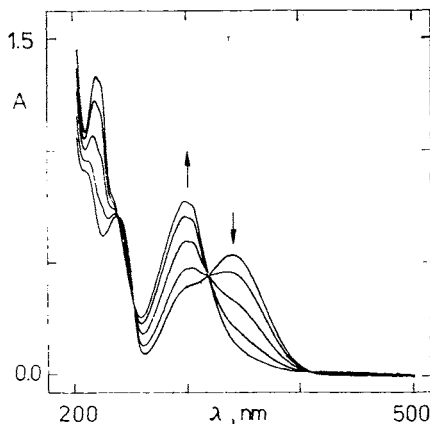


FIG. 1

Spectral changes during the irradiation of a solution of *I* in 50% aqueous tert-butanol in the presence of potassium cyanide (0.05 mol l^{-1}). Spectra were recorded at 0, 1, 3, 6, 10 and 20 min of irradiation time

anion in 50% aqueous tert-butanol (Table I). From the data it follows that the quantum yield increases with the increasing concentration of potassium cyanide and reaches a maximum at about 100-fold excess of the nucleophile. This indicates a bimolecular mechanism of the photoreaction which was found for example in the case of the alkaline photohydrolysis of 3,5-dinitroanisole⁴ (S_N2-3Ar^*).

Multiplicity of the reactive excited state was determined by quenching experiments using 2,4-hexadienoic acid as a selective triplet quencher¹⁷; the results are summarized in Table II. There is a significant quenching effect due to 2,4-hexadienoic acid which indicates the participation of triplet excited state. This conclusion is supported by the pronounced effect of oxygen, another selective triplet quencher, on photocyanation quantum yields, as can be seen from the data in Table I. On the

TABLE I

Quantum yield of the photocyanation of *I* ($1.25 \cdot 10^{-4} \text{ mol l}^{-1}$) in aerated (Φ_{Ox}) and argon saturated (Φ_{Ar}) 50% tert-butanol in dependence on the potassium cyanide concentration, [KCN]

10^3 [KCN] mol l^{-1}	Φ_{Ar}	Φ_{Ox}
0.50	0.075	0.023
0.55	0.079	0.025
0.63	0.090	0.028
0.71	0.098	0.032
0.83	0.111	0.037
1.00	0.133	0.043
1.25	0.151	0.052
1.66	0.175	0.066
2.50	0.216	0.094
5.00	0.247	0.142
10.0	0.294	0.202
25.0	0.315	0.268

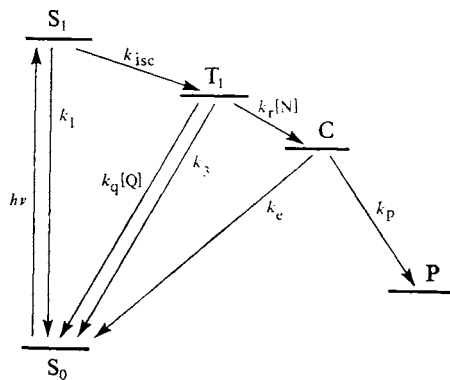
TABLE II

Quantum yield of the photocyanation of *I* ($1.25 \cdot 10^{-4} \text{ mol l}^{-1}$, 0.01 M-KCN) in 50% aqueous tert-butanol in dependence on the concentration of 2,4-hexadienoic acid, [HDA]

10^3 [HDA]^a	0.00	0.66	1.31	1.96	2.60	3.24	3.88	4.51
Φ	0.294	0.265	0.230	0.214	0.193	0.185	0.167	0.157

^a mol l^{-1} .

basis of the experimentally observed dependence of quantum yield on the nucleophile as well as quencher concentration we suggest that the photocyanation of *I* occurs by the mechanism described in Scheme 2.



SCHEME 2

The substrate molecule in its ground electronic state S_0 absorbs a light quantum and is thus transformed into the singlet excited state S_1 which undergoes either monomolecular deactivation (rate constant k_1) or forms the triplet excited state T_1 by intersystem crossing (k_{isc}). T_1 decays *via* the following three channels: monomolecular deactivation (k_3), bimolecular quenching process (k_q) due to interaction with the quencher molecule (Q) or a bimolecular reaction (rate constant k_r) with the nucleophile, N, leading to the formation of an intermediate complex C. This transient species either decomposes to educts (k_e), or can be eventually transformed to reaction products P (k_p). The application of the steady-state approximation on the proposed scheme leads to equation (1) which expresses the dependence of the reaction quantum yield on the concentrations of N and Q.

$$\Phi = \frac{k_p}{k_p + k_e} \frac{k_r[N]}{k_r[N] + k_q[Q] + k_3} \frac{k_{isc}}{k_{isc} + k_1} \quad (1)$$

Let us denote the efficiency of the productive transformation of C, $k_p/(k_p + k_e)$, as Γ and the efficiency of the triplet state formation, $k_{isc}/(k_{isc} + k_1)$, as Φ_{isc} . Then, at zero quencher concentration, the dependence of the reciprocal quantum yield Φ^{-1} on the reciprocal nucleophile concentration $[N]^{-1}$ is given by equation (2).

$$\Phi^{-1} = \Gamma^{-1} \Phi_{isc}^{-1} \left(1 + \frac{k_3}{k_r} [N]^{-1} \right) \quad (2)$$

Equation (2) describes a straight line in the coordinate system $\Phi^{-1} - [N]^{-1}$ with the intercept equal to $\Gamma^{-1}\Phi_{isc}^{-1}$ (equivalent to the reciprocal limiting quantum yield, Φ_{lim}^{-1} , at infinite nucleophile concentration) and with the slope $\Gamma^{-1}\Phi_{isc}^{-1}k_3/k_r$. Regression analysis of the experimentally determined dependence of Φ^{-1} on $[KCN]^{-1}$ (see also Fig. 2) using the values in Table I indeed gave a linear equation, $\Phi^{-1} = 5.27 \cdot 10^{-3}[KCN]^{-1} + 2.72$ ($r = 0.998$). The limiting quantum yield at infinite nucleophile concentration calculated from this empirical formula, Φ_{lim} , is equal to 0.368; it determines also the value of Φ_{isc} would Γ be hypothetically equal to unity. Conversely, from $\Phi_{isc} = 1.00$ it follows $\Gamma = 0.368$; in other words, both the quantities Φ_{isc} and Γ have their values in the range 0.368–1.00.

According to the Stern–Volmer analysis, the dependence of the relative reciprocal quantum yield on the quencher concentration $[Q]$ is described by equation (3), where Φ_0 corresponds to $[Q] = 0$.

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_q}{k_r[N] + k_3} [Q] \quad (3)$$

A linear regression analysis of the experimentally determined dependence of Φ on the concentration of 2,4-hexadienoic acid, $[HDA]$, gave the empirical formula $\Phi_0/\Phi = 1.00 + 193 [HDA]$ ($r = 0.998$, see Fig. 3).

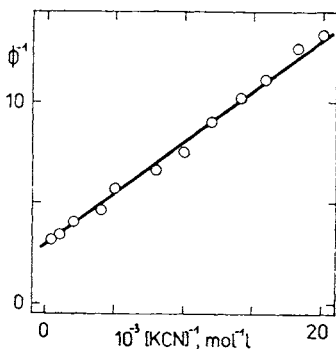


FIG. 2

Reciprocal quantum yield of photocyanation of I ($1.25 \cdot 10^{-4} \text{ mol l}^{-1}$), Φ^{-1} , in argon saturated tert-butanol–water (1 : 1, v/v) in dependence on the reciprocal potassium cyanide concentration, $[KCN]^{-1}$

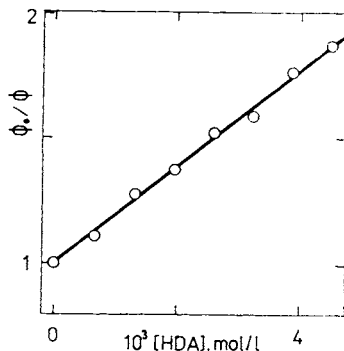


FIG. 3

Relative reciprocal quantum yield of photocyanation of I ($1.25 \cdot 10^{-4} \text{ mol l}^{-1}$, 0.01 M-KCN) in argon saturated tert-butanol–water (1 : 1, v/v), Φ_0/Φ , in dependence on the concentration of 2,4-hexadienoic acid, $[HDA]$

From the results of the quenching experiments, together with the dependence of Φ on $[\text{KCN}]$, the values of both k_r and k_3 could be evaluated would k_q be known. Quite often, the bimolecular quenching process is considered to be very fast, namely diffusion controlled. The rate constant of a diffusion controlled process in the medium of the viscosity η ($\text{kg m}^{-1} \text{s}^{-1}$) at the temperature $T(\text{K})$ can be estimated using a simple empirical formula¹⁸, $k_{\text{diff}} = 20\,000 T/\eta$. At 298 K and viscosity of the mixture water-tert-butanol 1 : 1 (v/v) equal to $3.5 \cdot 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ we get the estimated value of k_q $1.3 \cdot 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

The Stern-Volmer constant, K_{SV} , *i.e.* the coefficient at $[\text{Q}]$ in equation (3), can be written as $K_{\text{SV}} = 193 \text{ l mol}^{-1} = 1.3 \cdot 10^9 / (0.01k_r + k_3)$, where the concentration of the nucleophile in quenching experiments (0.01 mol l^{-1}) is utilized. On the other hand, k_r and k_3 are interrelated on the basis of the dependence of Φ^{-1} on $[\text{KCN}]^{-1}$ since k_3/k_r is equal to the slope to intercept ratio in the empirical formula describing

TABLE III

Dependence of quantum yield on solvent composition: photocyanation of I ($1.25 \cdot 10^{-4} \text{ mol l}^{-1}$, 0.05 M-KCN) in tert-butanol-water or methanol-water mixtures

% ROH	Φ	
	t-C ₄ H ₉ OH	CH ₃ OH
0	0.039	0.039
25	0.201	0.059
50	0.313	0.082
75	0.539	0.113
88	0.682	0.125

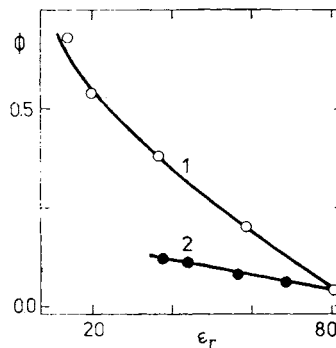


FIG. 4

Plot of the limiting quantum yield of photocyanation of I ($1.25 \cdot 10^{-4} \text{ mol l}^{-1}$, 0.05 M-KCN) in mixtures of tert-butanol-water (curve 1) and methanol-water (curve 2) against the relative dielectric permittivity of the mixtures

the linear function $\Phi^{-1} - [\text{KCN}]^{-1}$, $k_3/k_r = 1.94 \cdot 10^{-3} \text{ mol l}^{-1}$. Solving the equations we obtain $k_r = 5.6 \cdot 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_3 = 1.1 \cdot 10^6 \text{ s}^{-1}$. The life-time of triplet excited 3,4-dimethoxy-1-nitrobenzene as determined by kinetic methods is therefore $k_3^{-1} = 0.9 \cdot 10^{-6} \text{ s}$ in 50% aqueous tert-butanol. Bimolecular rate constant for the interaction of the triplet excited state with cyanide anion is not much lower (by the factor 0.43) than the rate constant for diffusion controlled quenching. For comparison⁴, the interaction of triplet 3,5-dinitroanisole with hydroxide anion in water is even as fast as the diffusion ($k_r = 26 \cdot 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$).

We found that the limiting quantum yield of the photocyanation of *I* ($1.25 \cdot 10^{-4} \text{ mol l}^{-1}$) in anaerobic media (0.05M-KCN) is strongly dependent on the water-tert-butanol mixture composition. To gain more information concerning the influence of solvent on the quantum yield of photocyanation of *I*, we have also determined the values of Φ_{lim} (0.05M-KCN) for the system water-methanol (see the data in Table III).

As for the solvent properties influencing Φ , viscosity can probably be excluded since it has a local maximum at about 25% tert-butanol¹⁹ ($5 \cdot 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$) and decreases on going to either of the pure component (water $1 \cdot 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$, tert-butanol $3 \cdot 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$), while the quantum yield exhibits a monotonous increase with the increasing amount of the latter. On the other hand, polarity as measured by the relative dielectric permittivity, ϵ_r , is among the solvent properties which depend linearly on the solvent mixture composition²⁰⁻²² thus representing a factor possibly responsive for the pronounced solvent effect. Nevertheless, as can be seen from Fig. 4, all the experimental data could not be explained by polarity alone and additional factors must be operative, as for example a preferential solvation of the aromatic substrate by organic co-solvent or its influence on hydrogen bond strength⁴.

We can conclude that the kinetic study of nucleophilic photosubstitution reactivity of 3,4-dimethoxy-1-nitrobenzene gave information concerning the properties of triplet excited state of the substrate. The excited state life-time of 0.9 μs is sufficiently high for the bimolecular reactions to occur. Its reactivity with the nucleophile is rather high, the bimolecular rate constant of the reaction approaching the value of the rate constant for diffusion. These are obviously the properties which enabled a successful attempt to utilize 3,4-dimethoxy-1-nitrobenzene as a reactive moiety in the photoaffinity labelling of a biomolecule⁶.

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