

OXIDATIVE REARRANGEMENT OF *o*-FUCHSONE TO 2,2-DIPHENYL-1,3-BENZODIOXOL*

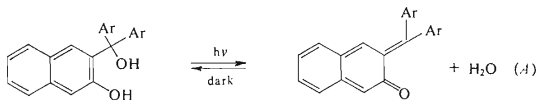
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The photo-decolouration of *o*-fuchsonone is caused by [8 + 2] cycloaddition of singlet oxygen to the quinonoid trienone π -system. The arising 1,2,3-trioxanaphthalene undergoes further fragmentations and recyclizations to give 1,3-benzodioxol. The course of this reaction was investigated using fuchsones I–IV as substrates and hydrogen peroxide and tert-butyl hydroperoxide as oxidants. The thermolabile epoxy ketone XV was identified as the key intermediate.

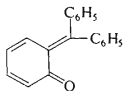
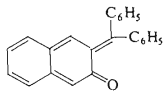
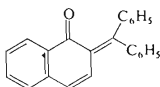
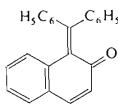
Since Marckwald's observation¹ in 1899 that some colourless naphthalene derivatives became coloured on exposure to light and that this light-induced colouration disappeared again in the dark many systems exhibiting similar behaviour (*i.e.* photochromism) have been discovered². Photochromism has been also observed with many triphenylmethane derivatives³ the most important among them being triarylacetonitriles, triarylmethanesulfonates and triarylmethanols. In these compounds the photoexcitation is followed by a cleavage of the C—X bond which results in coloured, resonance stabilized, triarylmethyl cations. However, if *e.g.* a triarylmethanol molecule contains at least one phenolic *o*-hydroxy group, then the coloured species is no more a carbocation but an uncharged quinonoid species, *o*-fuchsonone⁴.



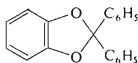
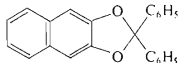
The reverse reaction the mechanism of which has been thoroughly investigated with some quinone methides⁵ could be accomplished either thermally (dark reaction) or by irradiation at a wavelength corresponding to the absorption of the coloured form (photobleaching). The photochromic system (A) complemented a substance binding the liberated water might be of a practical value provided that it was suffi-

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ciently stable with respect to environmental conditions, particularly to atmospheric oxygen. As the most reactive component of the system considered is represented by *o*-fuchsones, whose reactions with oxidants have not been hitherto described, we decided to investigate in detail the quinonoid compounds *I–IV*.

*I**II**III**IV*

6-Benzhydrylidene-2,4-cyclohexadien-1-one (benzofuchsones) (*I*), 4-benzhydrylidene-1,5,7,9-tetraen-3-one (naphthofuchsones) (*II*) and naphthofuchsones *III* and *IV* are accessible by photolytic dehydration in minute quantities only. Therefore, we prepared these compounds by thermal^{6,7} or base-catalyzed dehydrohalogenation of the corresponding triarylmethylchlorides in non-polar solvents. Aeration of the benzene solutions of fuchsones *I–IV* in diffuse daylight (or in the light of fluorescent tube) resulted in a rapid conversion ($\tau_{1/2} \sim 10$ min) of compounds *I* and *II* into colourless products while compounds *III* and *IV* remained unchanged. Thus *o*-fuchsones *I* afforded a product the melting point and IR spectrum of which were identical with those of the authentic sample of 2,2-diphenylbenzo[α]-1,3-dioxol (*V*). Under identical conditions the naphthofuchsones *II* afforded, almost quantitatively, a product whose analytical and spectral data indicated the structure *VI*. The assignment of this structure was confirmed by a hydrolysis of the compound with hot sulfuric acid to 2,3-dihydroxynaphthalene and benzophenone.

*V**VI*

If the solutions of fuchsones *I* and *II* were aerated in the dark or irradiated in carefully deoxygenated solutions the decolouration proceeded slowly ($\tau_{1/2} \sim 5$ h).

Having considered the number of products contained in the almost colourless solutions (neither dioxol *V* nor *VI* were found) we deduced the *o*-fuchsones *I* and *II* underwent other competitive reactions in the dark being at least by an order of magnitude slower when compared with photooxidation.

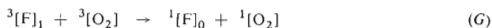
The aforementioned experiments together with the product structures clearly show that oxygen participates in the bleaching reactions of *o*-fuchsones *I* and *II*. As the fuchsones ground state is a singlet and a reaction of the triplet oxygen with a substrate in the singlet state is spin-forbidden⁸ (equation (B)), only two reactions can be considered for spin-allowed interactions. In one of them singlet oxygen reacts with fuchsones

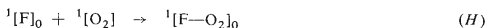


in the ground state (equation (C)), whereas in the latter both components react in triplet states (equation (D)).



The following experiments were carried out in order to make a decision between these alternative mechanisms. The photobleaching of the fuchsones *I* in dichloromethane solution in the presence of 10 mol % of 1,4-diazabicyclo[2,2,2]octane (DABCO) proceeded very slowly when compared with the control experiment. This finding supports the pathway (C), because DABCO is well-known singlet oxygen quencher⁹. Nevertheless, we cannot exclude that DABCO, similarly to other tertiary amines^{10,11}, could quench the fuchsones triplet state, making impossible a decision to be made between the primary steps (C) and (D). Therefore we utilized the ability of 2,6-ditert-butyl-4-methylphenol (*VII*) to inhibit intermolecular radical processes to which the reaction (D) belongs beyond dispute. Since the fuchsones *I* photooxidation was not perceptibly retarded even in the presence of 15 mol % of the phenol *VII* the primary step (D) could be excluded with high probability. For the photooxidation of the fuchsones *I* and *II* we suggest the following reaction sequence (Scheme 1) in which the fuchsones act simultaneously as a sensitizer and a substrate. The scheme does not involve any photo-physical processes leading to deactivation of excited molecules.





SCHEME 1

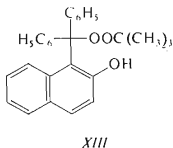
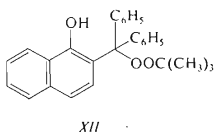
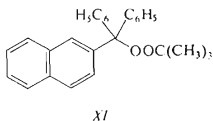
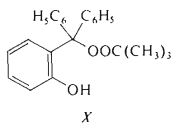
It is obvious that the ${}^1[\text{F}-\text{O}_2]$ species cannot have properties of a charge transfer complex but it must contain oxygen covalently bound to the *o*-fuchsonone molecule; hence, we consider this species as the first photooxidation intermediate. The dioxetane *VIII* (the product of singlet oxygen $[2 + 2]$ cycloaddition to exocyclic fuchsonone double bond) can be safely excluded from consideration using the following arguments. The O—O and C—C bonds within the four-membered dioxetane ring are



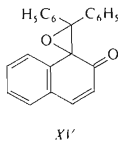
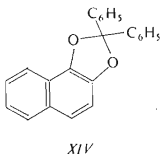
rather weak and cleave readily to give carbonyl compounds (in this case *o*-benzoquinone and benzophenone). However, none of these compounds was found in products of photooxidation of the *o*-fuchsonone *I*. Moreover, it is almost impossible to rationalize mechanistically the rearrangement of the dioxetane *VIII* to the dioxol *V*. The idea, which seems much more attractive, operates with the $[8 + 2]$ cycloaddition reaction between singlet oxygen and strictly planar *cisoid* arrangement of the trienone *I*, resulting in a 4,4-diphenyl derivative of the hitherto unknown 4*H*-1,2,3-trioxanaphthalene *IX*. This reaction represents an extension of the well-known cycloadditions of singlet oxygen^{12,13} from dienes to heterodienes. The smooth progress of this reaction is apparently controlled with the stability of products¹⁴ caused by a considerable gain in resonance energy. The validity of this conclusion is supported by the non-reactivity of fuchsones *III* and *IV*. The trioxanaphthalene *IX* could not be detected although the benzaldehyde hydrotrioxide¹⁵, a compound with three oxygen atoms in the open chain, is fairly stable.

Since all attempts to identify any intermediates in the reaction of fuchsones *I* and *II* with singlet oxygen were unsuccessful, we tried to get some insight into the reaction mechanism with the aid of model reactions. We made use of a high reactivity of quinone methides with nucleophiles¹⁶ and subjected the *o*-fuchsonone *I* to a reaction with hydroperoxide anion in buffered acetonitrile solution¹⁷. However, the sole product isolated in high yield corresponded again to benzodioxol *V*. Identical result was obtained with a reaction of *o*-fuchsonone *I* with sodium tert-butyl peroxide in me-

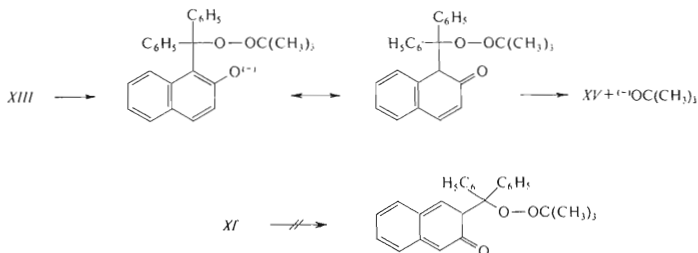
thanol¹⁸. Only the addition reaction of tert-butyl hydroperoxide to fuchsonone *I* in benzene has proved successful affording a stable compound *X*. (The structure was assigned on the basis of IR spectra and elemental analysis). Under the same conditions the fuchsones *II–IV* afforded analogous well characterized peroxides *XI–XIII*.



Since all the attempted preparations of the peroxide *X* in basic media resulted invariably in a formation of dioxol *V*, it was clear that the intermediate adduct was destroyed in the presence of a base. Due to this fact we subjected the acetonitrile solutions of peroxides *X–XIII* to triethylamine. As expected, the peroxide *X* afforded benzodioxol *V* and peroxides *XII* and *XIII* were converted to naphthodioxol *XIV*. On the other hand triethylamine had no effect on the stability of peroxide *XI*. Identical results were obtained also with other bases (piperidine, sodium methoxide). Spectrophotometric investigation of the kinetics of the triethylamine-catalyzed rearrangement revealed a presence of intermediates the absorption maxima of which were shifted towards shorter wavelengths as compared with the corresponding fuchsones. In the case of peroxide *XIII* we succeeded in isolating this intermediate by lowering the reaction temperature to -10°C and using flash chromatography¹⁹ for its isolation. Analysis of the spectral data resulted unequivocally in the structure *XV*.

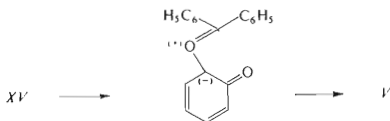


A plausible mechanism of the formation of the epoxy ketone *XV* from the peroxide *XIII* involves an attack of weakly electrophilic peroxide $O_{(1)}$ oxygen by the C-anion of the mesomeric phenolate ion accompanied by the $O_{(1)}-O_{(2)}$ bond cleavage. Both these processes operate simultaneously (Scheme 2). This mechanism is supported by the fact that the peroxide *XI*, which is not capable to generate a carbanion at $C_{(3)}$ of the naphthalene skeleton, is stable towards bases.



SCHEME 2

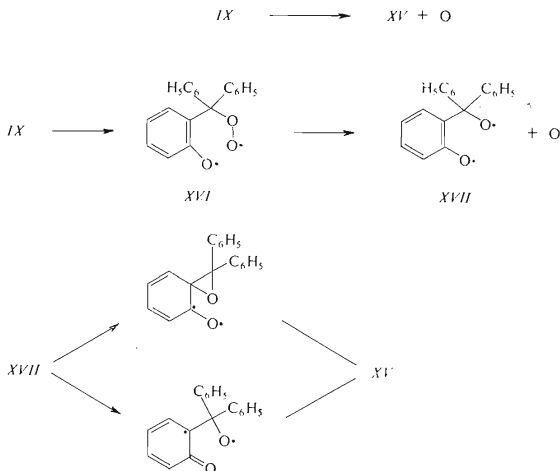
The epoxy ketone *XV* is of low thermodynamic stability and rearranges to the naphthodioxol *XIV* slowly at room temperature and rapidly at its melting point. This rearrangement can be regarded as an electrocyclic symmetry allowed $[\pi 4s + \pi 2s]$ reaction in which the necessary four electron system is formed by rupture of the oxirane C—C bond²⁰. Rearrangements of this type are known for structurally related epoxy ketones in other, mainly oxidative, reactions. Thus, epoxidation of the naphthofuchsones *II* with *m*-chloroperoxybenzoic acid leads directly to the naphthodioxol *VI*, periodic acid oxidation²¹ of (2-hydroxyphenyl)diphenylmethanol affords the benzo-dioxol *V* and, finally, addition of carbene²² to 3,4-dichloro-1,2-benzoquinone gives 3,4-dichloronaphtho[*b*]-1,3-dioxol together with its precursor 5,6-dichloro-7,8-benzo-1-oxaspiro[2,5]deca-5,7-dien-4-one.



SCHEME 3

The results of model experiments can be used for the outline of the fuchsones photo-oxidation mechanism provided that the following assumptions are made: 1) The

first intermediate must contain the O—O bond. 2) The process leading from peroxide to dioxol must be intramolecular. 3) This process must be either synchronous or radical but not ionic. The validity of these assumptions is sufficiently proved by the nature of the reacting species together with the negative results of cross experiments and the facile photooxidation of the naphthofuchsone *II*. The intramolecular decomposition of trioxanaphthalene *IX* (either synchronous or stepwise), which involves biradical intermediates, must afford in both cases the product of intramolecular cyclisation, the epoxy ketone *XV* (Scheme 4).



SCHEME 4

Of both the possible pathways we favour the single-step process *IX*—*XV* characterized by the more favourable entropy. It is worth mention that both the suggested mechanisms operate with a formation of atomic oxygen. Irrespective whether it exists in 1D or 3P state, its electronic structure as well as other properties closely resemble those of carbene and as such it can epoxidize directly the fuchsone exocyclic double bond.

In conclusion, we may state that those *o*-hydroxyaryldiphenylcarbinols are not useful as photochromic compounds, which on transition to their coloured forms suffer a complete loss of aromatic resonance energy.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Samples for elemental analyses were dried for 7 h at 13 Pa at room temperature. IR Spectra were recorded on IR-20 (Carl Zeiss, Jena) spectrophotometer and UV spectra on Specord UV-VIS (Carl Zeiss, Jena) spectrophotometer. Mass spectra were measured on AEI MS 902 (70 eV, source temperature 110–230°C) instrument.

Preparation of 6-Benzhydrylidene-2,4-cyclohexadien-1-one (*I*) and 4-Benzhydrylidenebicyclo[4.4.0]deca-1,5,7,9-tetraen-3-one (*II*)

A) Dry hydrogen chloride was introduced at room temperature for 1–3 min into a stirred solution of diphenyl(2-hydroxyphenyl)methanol²³ (276 mg, 1 mmol) in benzene (15 ml) containing anhydrous magnesium sulfate (800 mg). The mixture was decanted and the remaining magnesium sulfate washed with benzene (3 × 3 ml). The benzene solution of diphenyl(2-hydroxyphenyl)methyl chloride was cooled to 0°C and stirred for 30 min under nitrogen with DEAE Spheron²⁴ (1 g, capacity 2 mequiv/g). Spheron was filtered off, washed with benzene (3 × 1 ml) and the filtrate was made up to 10 ml. The red solution of the fuchsones *I* exhibited λ_{\max} 424 nm (benzene); its concentrated solutions decolorized rapidly during attempted isolation.

B) The solution of the fuchsones *II* (λ_{\max} 383 nm, benzene) was prepared from diphenyl(2-hydroxynaphthyl)methanol as described under *A*.

Photooxidation of the Fuchsones *I* and *II*

A) A solution of the fuchsones *I* (0.1 mmol) in benzene (5 ml) placed in a quartz cell was aerated under simultaneous irradiation with the RVL 125 fluorescent tube. The end of reaction was indicated by a complete decoloration of the solution. Evaporation of the solvent and crystallization of the residue (27 mg) from light petroleum afforded 2,2-diphenylbenzo[*d*]-1,3-dioxol (*V*), m.p. 89–91°C (reported²⁶ m.p. 93°C).

B) A solution of the fuchsones *II* (0.1 mmol) in benzene (5 ml) in a Pyrex flask was exposed to daylight under stirring. After decoloration the solution was taken down and the residue (31 mg) crystallized from the ether–light petroleum mixture. 2,2-Diphenylinaphtho[2,3-*d*]-1,3-dioxol (*VI*) exhibited m.p. 150–152°C. For C₂₃H₁₆O₂ (324.3) calculated: 85.16% C, 4.97% H; found: 85.41% C, 4.96% H. IR Spectrum (tetrachloromethane): 1 284 cm⁻¹.

C) Benzene solution of the fuchsones *I* ($1 \cdot 10^{-4}$ mol l⁻¹) containing DABCO ($1 \cdot 10^{-5}$ mol l⁻¹) was irradiated as described under *A*. The kinetic profile of the reaction was monitored spectrophotometrically at 424 nm ($\tau_{1/2} \sim 5$ h).

D) Benzene solution of the fuchsones *I* ($1 \cdot 10^{-4}$ mol l⁻¹) containing *VII* ($1.5 \cdot 10^{-5}$ mol l⁻¹) was irradiated as described under *A*. The kinetic profile of the reaction was monitored spectrophotometrically at 424 nm ($\tau_{1/2} \sim 10$ min).

Reaction of the Fuchsones *I* with Hydrogen Peroxide

A solution of the fuchsones *I* (1.5 mmol) in acetonitrile (15 ml) was mixed with 30% hydrogen peroxide (0.3 g, 2.6 mmol) and solutions of sodium hydrogenphosphate (0.2 g) in water (1.5 ml) and sodium hydroxide (0.06 g) in water (1.5 ml) were added. The mixture was stirred under nitrogen till it became colourless. Acetonitrile was evaporated and the aqueous solution extracted

with ether. The extract was taken down and the residue chromatographed on silica gel (50 g, ether–light petroleum) affording as the main product the dioxol *V* (395 mg), m.p. 90–91°C and a small quantity of 2-hydroxytriphenylmethanol, m.p. 142°C (reported²³ m.p. 140.5°C).

Reaction of *o*-Fuchsones *I* with Sodium Tert-Butyl Hydroperoxide

A solution of the fuchsones *I* (1 mmol) in acetonitrile (10 ml) was added at room temperature under nitrogen to a stirred solution of sodium tert-butyl hydroperoxide (0.3 g, 3 mmol) in methanol (15 ml). After decoloration the mixture was worked up affording the dioxol *V* (263 mg), m.p. 90–92°C, as the sole product.

Reaction of Fuchsones *I–IV* with Tert-Butyl Hydroperoxide

A solution of tert-butyl hydroperoxide (240 mg, 3 mmol) in benzene (2 ml) was added to a stirred solution of the fuchsones *I* (0.5 mmol) in benzene (15 ml). The mixture was allowed to stand at room temperature until it became colourless. The excess of solvent was distilled off *in vacuo* and the residue was chromatographed on silica gel (30 g, light petroleum). Diphenyl(2-hydroxyphenyl)methyl tert-butyl peroxide (*X*), m.p. 89–91°C (hexane). For $C_{23}H_{24}O_3$ (348.4) calculated: 79.28% C, 6.94% H; found: 79.66% C, 6.94% H. IR Spectrum (tetrachloromethane): 1 196, 1 243, 1 365, 1 389, 3 430 cm^{-1} . Diphenyl(3-hydroxy-2-naphthyl)methyl tert-butyl hydroperoxide (*XI*) (172 mg, 86.0%), m.p. 149–151°C (ether). For $C_{27}H_{26}O_3$ (398.5) calculated: 81.38% C, 6.58% H; found: 80.96% C, 6.52% H. IR spectrum (chloroform): 1 367, 1 391, 3 405 cm^{-1} . Diphenyl(1-hydroxy-2-naphthyl)methyl tert-butyl peroxide (*XII*) (165 mg, 82.5%), oil. For $C_{27}H_{26}O_3$ (398.5) calculated: 81.38% C, 6.58% H; found: 82.87% C, 6.61% H. IR Spectrum (tetrachloromethane): 1 195, 1 231, 1 366, 1 390, 3 365 cm^{-1} . Diphenyl(2-hydroxy-1-naphthyl)methyl tert-butyl hydroperoxide (*XIII*) (175 mg, 87.5%), m.p. 99–102°C (hexane). For $C_{27}H_{26}O_3$ (398.5) calculated: 81.38% C, 6.58% H; found: 82.09% C, 6.52% H. IR Spectrum (tetrachloromethane): 1 194, 1 228, 1 366, 1 390, 3 375 cm^{-1} .

Rearrangements of the Peroxy Phenols *X*, *XII* and *XIII*

The peroxy phenol (0.25 mmol) was dissolved in acetonitrile (5 ml) at room temperature and the 5% solution (300 μ l) of triethylamine in acetonitrile was added. After several minutes the solvent was distilled off *in vacuo* and the corresponding dioxol was isolated in 97–99% yield. 2,2-Diphenylbenzo[*d*]-1,3-dioxol (*V*), m.p. 89–91°C. 2,2-Diphenylnaphtho[1,2-*d*]-1,3-dioxol (*XIV*), m.p. 101 to 103°C (light petroleum). For $C_{23}H_{16}O_2$ (324.3) calculated: 85.16% C, 4.97% H; found: 85.38% C 5.04% H. IR Spectrum (tetrachloromethane): 1 286 cm^{-1} .

2,2-Diphenylnaphtho[2,3-*d*]-1,3-dioxol (*VI*)

m-Chloroperoxybenzoic acid (345 mg, 2 mmol) in benzene (10 ml) was added to a solution of the naphthofuchsones *II* (1 mmol) in benzene (10 ml). Filtration through alumina (2 g, Alumina Woelm B, act. I) afforded naphthodioxol *VI*, m.p. 150–152°C (ether–light petroleum). For $C_{23}H_{16}O_2$ (324.3) calculated: 85.16% C, 4.97% H; found: 85.41% C, 4.96% H. IR Spectrum (tetrachloromethane): 1 284 cm^{-1} .

Preparation of the Epoxy Ketone *XV*

The 5% solution of triethylamine in acetonitrile (0.3 ml) was added to a cooled (–10°C) solution of the peroxy phenol *XII* (100 mg) in acetonitrile (5 ml). After about thirty seconds

the mixture was subjected to flash chromatography¹⁹ yielding 94% of 2,2-diphenyl-6,7-benzo-1-oxaspiro[2,5]deca-4,6-dien-8-one (XV), m.p. 66–69°C (pre-heated block). IR Spectrum (acetonitrile): 1682 cm⁻¹; (tetrachloromethane): 1692 m⁻¹. Mass spectrum: 324·1141 (for C₂₃H₁₆O₂ calculated: 324·1150).

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