

INTERMOLECULAR CYCLIZATION OF *o*-FUCHSONES*

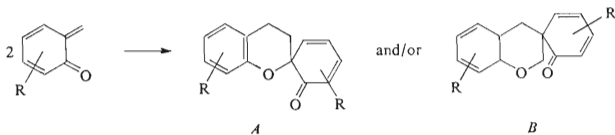
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o-Fuchsones formed by dehydrohalogenation of *o*-hydroxyaryl(diaryl)methyl chlorides with tertiary amines undergo a cyclization to eight-membered dimers of the type head to tail. The dimerization reaction is catalyzed by tertiary amines hydrochlorides involving very likely triaryl-methyl cation as intermediates.

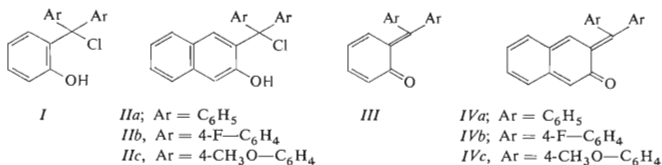
The compounds containing an *o*-quinoid moiety exhibit a wide range of chemical transformations¹. Extremely high reactivity is characteristic for *o*-quinodimethanes and *o*-quinone methides which cannot be isolated if not stabilized by suitable substitution. *o*-Quinone methides readily form 1,8-adducts with nucleophiles², and undergo cycloaddition reactions with dienophiles³ or singlet oxygen⁴. At the absence of any such reactive component the *o*-quinone methides dimerize by [4 + 2] mechanism^{5,6}. In any case, the dimers thus formed exhibit a structure of spirodienones formed by head to head (*A*) or head to tail (*B*) type of cycloaddition reaction (Scheme 1).



SCHEME 1

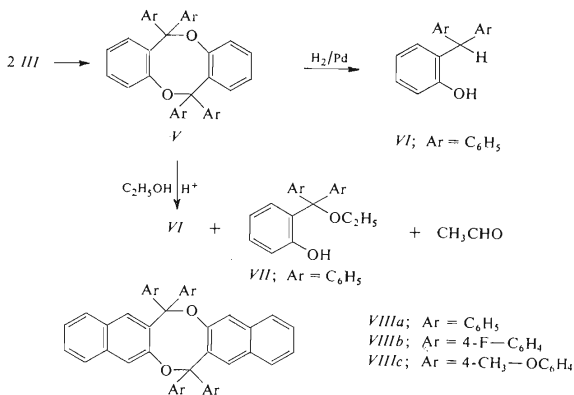
In the course of our studies on photooxidative reactions of *o*-fuchsones⁴ we realized that the trienone system of these compounds was undergoing further reactions unlikely participated with any other agent. These reactions were reinvestigated for two reasons: first, the reaction course was dependent on the type and amount of the base used to release the *o*-fuchsones *III* and *IV* from the triarylmethyl chlorides *I* and *II* and second, the properties of products were different from those expected.

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The *o*-fuchsones were released from triarylmethyl chlorides using a polymeric base, DEAE - Spheron (diethylaminoethyl derivative of a macroreticular polymer based on hydroxyalkyl methacrylate)⁷ or an equivalent amount of triethylamine. At the presence of oxygen and under simultaneous irradiation the fuchsones were readily transformed to 2,2-diphenyl-1,3-dioxoles. At the absence of oxygen or in the darkness a slow reaction (compared to photooxidation) was taking place resulting however also in a destruction of the fuchsones chromophore. In any case we isolated only one compound from the reaction medium in an almost theoretical yield. Melting points of these compounds were high. Mass spectra showed low intensity molecular ions the masses of which were twice as large than those of the starting *o*-fuchsones. The base peak corresponded to the original fuchsones with its composition. On the basis of the reported precedents^{5,6} we supposed the *o*-fuchsones to undergo a reaction of the Diels-Alder type and the dimers thus formed to have a general structure either *A* or *B* (Scheme 1). This preliminary structural assignment might be readily eliminated on the basis of additional spectral data. The dimer obtained from the benzofuchsones *III* was transparent above 300 nm. However, any [4 + 2] addition reaction must generate a conjugated system which is detectable above 300 nm and contains a carbonyl group recognizable by spectroscopy. The only frequencies detected in the IR spectra corresponded to aromatic system and aryloxy bond. Moreover, the [4 + 2] type of addition reaction was excluded by a shape of NMR spectrum which has clearly shown that the molecule is symmetric lacking any unsaturation and any other protons additional to those belonging to the aromatic cycle. The most probable structure compatible with all the spectral data corresponds to tetraphenyl-dibenzo-3,7-dioxo-1,5-cyclooctadiene (*V*).

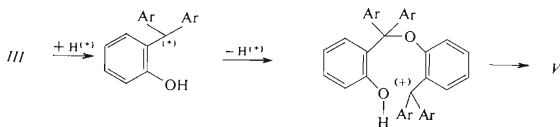
The correctness of this structure was proved by chemical degradations (Scheme 2). The dimer *V* absorbed 2 mol of hydrogen upon hydrogenation on a palladium catalyst and yielded almost theoretical amount of diphenyl(2-hydroxyphenyl)methane⁸ (*VI*). By the action of ethanolic solution of *p*-toluenesulfonic acid the dimer *V* was converted into a mixture of triarylmethane *VI* and diphenyl(2-hydroxyphenyl)-ethoxymethane (*VII*). The presence of acetaldehyde in the reaction medium was proved by dinitrophenylhydrazine. The same solvolytic reaction applied to dimers *VIIIa* - *VIIIc* has led to analogous results.



SCHEME 2

The formation of the earlier reported spirodimers *A* and *B* may be characterized as a concerted symmetry allowed $[\pi 8s + \pi 2s]$ cycloaddition reaction. The thermal cyclization not violating the Woodward-Hoffmann rules⁹ and leading to eight-membered heterocycle *V* would have to proceed by either $[\pi 8s + \pi 8a]$ or radical mechanism. The first mechanism may be eliminated on the basis of stereoelectronic considerations. The second mechanism, frequently taking place with dimerization of *o*-quinodimethanes¹⁰, may be rejected as well due to the fact that the *o*-fuchstone *IVa* affords no ESR signal.

Two additional pathways of the $[8 + 8]$ dimer formation can be considered. We suppose that the tertiary base hydrochloride which is present in the reaction medium protonates the considerably basic carbonyl oxygen atom of the fuchstone at the first stage. Then the triarylmethyl cation thus formed attacks either the phenolic oxygen atom of the same species or the carbonyl oxygen atom of the fuchstone (Scheme 3). Cyclization of the phenoxy cation to the dimer proceeds then in a trivial manner.



SCHEME 3

The other possible pathway is interesting from the theoretical viewpoint as it starts with the assumption of a high polarizability of *o*-quinone methides. The molecules of this type may react in a form conforming best to the addendum¹¹ but the reaction course cannot certainly be concerted. However, this variant disagrees with the observation that either an excess of triethylamine or an immediate filtering off the DEAE — Spheron from the reaction medium causes a complete inhibition of the [8 + 8] dimers formation.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Samples for elemental analyses were dried for 8 h at laboratory temperature at 13 Pa. IR Spectra were measured on IR-20 (Carl Zeiss, Jena) spectrophotometer and UV spectra on Specord UV-VIS (Carl Zeiss, Jena) spectrophotometer. Mass spectra were recorded on AEI MS 902 instrument (70 eV, source temperature 110–230°C). ¹H NMR Spectra were measured on Varian HA-100 spectrometer in deuteriochloroform using tetramethylsilane as an internal standard.

Preparation of Dimers *VIIIa*–*VIIIc*

The necessary triarylmethanols were obtained by reaction of methyl esters of 2-hydroxybenzoic acid or 3-hydroxy-2-naphthoic acid with Grignard agents prepared from bromobenzene, 4-fluorobromobenzene and 4-bromoanisole.

Diphenyl(2-hydroxyphenyl)methanol (87%), m.p. 142°C (ref.¹² 142°C). Diphenyl(3-hydroxy-2-naphthyl)methanol (81%), m.p. 182–183°C (ref.¹² 181–182°C). Bis(4-fluorophenyl)(3-hydroxy-2-naphthyl)methanol (78%), m.p. 151–153°C (ether–light petroleum). For C₂₃H₁₆F₂O₂ (362.4) calculated: 76.23% C, 4.45% H, 10.48% F; found: 76.17% C, 4.48% H, 10.42% F. IR Spectrum (tetrachloromethane): 3 425, 3 560, 3 598 cm⁻¹. Mass spectrum: M⁺ 362. Bis(4-methoxyphenyl)(3-hydroxy-2-naphthyl)methanol (92%), m.p. 152–154°C (benzene). For C₂₅H₂₂O₄ (386.4) calculated: 77.70% C, 5.74% H; found: 76.67% C, 5.68% H. IR Spectrum (tetrachloromethane) 3 405, 3 600 cm⁻¹. Mass spectrum: M⁺ 386.

Triarylmethyl chlorides were prepared from the corresponding triarylmethanols by the action of hydrogen chloride⁴.

The dimers *VIIIa*–*VIIIc* were prepared by stirring the benzene (10 ml) solutions of the corresponding triarylmethyl chlorides (1 mmol) with triethylamine (114 μl, 1 mmol) or DEAE — Spheron (1 g, 2 mequiv.) at laboratory temperature till decoloration. The usual work-up procedure afforded:

1,2,5,6-*Dibenzo*-3,7-*dioxa*-4,4,8,8-*tetraphenyl*-1,5-*cyclooctadiene* (V), m.p. 274–276°C (ether). For C₃₈H₂₈O₂ (516.6) calculated: 88.34% C, 5.46% H; found: 88.41% C, 5.41% H. IR Spectrum (KBr pellet) 1 234 cm⁻¹. Mass spectrum: M⁺ 516, *m/e* 258 (base peak). 1,2,5,6-*Dinaphtho*[*b*]-3,7-*dioxa*-4,4,8,8-*tetraphenyl*-1,5-*cyclooctadiene* (*VIIIa*), m.p. 289–291°C (ether). For C₄₆H₃₂O₂ (616.7) calculated: 89.58% C, 5.23% H; found 89.47% C, 5.20% H. Mass spectrum: M⁺ 616, *m/e* 308 (base peak).

1,2,5,6-*Dinaphtho*[*b*]-3,7-*dioxa*-4,4,8,8-*tetra*(4-*fluorophenyl*)-1,5-*cyclooctadiene* (*VIIIb*), m.p. 279 to 281°C (ether–light petroleum). For C₄₆H₂₈F₄O₂ (688.7) calculated: 80.22% C, 4.10% H, 11.03% F; found: 80.31% C, 4.07% H, 11.08% F. Mass spectrum: M⁺ 688, *m/e* 344 (base peak).

1,2,5,6-Dinaphthyl[b]-3,7-dioxa-4,4,8,8-tetra-(4-methoxyphenyl)-1,5-cyclooctadiene (VIIIc), m.p. 234–236°C (benzene–light petroleum). For $C_{50}H_{40}O_6$ (736.8) calculated: 81.50% C, 5.47% H; found: 81.68% C, 5.45% H. IR Spectrum (tetrachloromethane) $1\ 252\text{ cm}^{-1}$. Mass spectrum: M^+ 736, m/e 368 (base peak).

Ethanolysis of the Dimer V

The dimer V (104 mg, 0.25 mmol) was dissolved in ethanol (20 ml) containing *p*-toluenesulfonic acid (2 mg). After staying for 24 h at laboratory temperature ethanol was taken down *in vacuo* and the residue chromatographed on silica gel (12 g, light petroleum–ether). Diphenyl(2-hydroxyphenyl)ethoxymethane (VII) (62 mg), m.p. 101–103°C (light petroleum) was isolated from first fractions. For $C_{21}H_{20}O_2$ (304.4) calculated: 82.87% C, 6.62% H; found: 82.59% C, 6.68% H. IR Spectrum (tetrachloromethane) $3\ 345\text{ cm}^{-1}$. Mass spectrum: M^+ 304, m/e 258 (base peak). The following fractions afforded 2-benzhydrylphenol (38 mg), m.p. 122–124°C (ref.⁸ 122 to 123°C).

Hydrogenation of the Dimer V

The dimer V (104 mg, 0.25 mmol) was dissolved in ethyl acetate (5 ml) and, after adding the suspension of prehydrogenated Pd catalyst (about 10 mg), reduced with hydrogen at laboratory conditions. The hydrogenation reaction stopped spontaneously after consumption of 10.8 ml H_2 (0.48 mmol). After removal of catalyst and solvent 2-benzhydrylphenol was obtained (91 mg) which exhibited m.p. 123–124°C (n-hexane).

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REFERENCES

1. Grünanger P. in the book: *Methoden der Organischen Chemie* (Houben-Weyl) (Ch. Grundman, Ed.), Vol. VII/3b. Thieme, Stuttgart 1979.
2. Padwa A., Dehm D., Oine T., Lee G. A.: *J. Amer. Chem. Soc.* **97**, 1837 (1975).
3. Brougidou J., Christol H.: *C. R. Acad. Sci. Ser. C257*, 3149 (1963).
4. Pišová M., Souček M.: This Journal, in press.
5. Cook C. D., Butler L. C.: *J. Org. Chem.* **34**, 227 (1969).
6. Jurd L.: *Tetrahedron* **33**, 163 (1977).
7. Mikeš O., Štrop P., Zbrožek J., Čoupek J.: *J. Chromatogr.* **119**, 339 (1976).
8. Baeyer A.: *Justus Liebigs Ann. Chem.* **354**, 152 (1907).
9. Woodward R. B., Hoffmann R.: *The Conservation of Orbital Symmetry*. Verlag Chemie, Weinheim 1970.
10. Bell T. W., Bowes C. M., Sondheimer F.: *Tetrahedron Lett.* **1980**, 3299.
11. Epitotis N. D.: *J. Amer. Chem. Soc.* **94**, 1935 (1972).
12. Andersen L. C., Thomas D. G.: *J. Amer. Chem. Soc.* **65**, 234 (1943).

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