On the Photochemical Dimerization of Some 5-Substituted 2-Styryl-4-pyrones. The Effect of 5-Hydroxy- / 5-Methoxy- Substitution

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Irradiation of styryl-4-pyrones **1a-1d** or **2a-2e** (6-9 x 10^{-3} *M*, methanol solution) with filtered (RAYONET photochemical reactor, 300 nm) or unfiltered uv-light (high-pressure mercury arc lamp) under aerobic conditions led mainly to dimeric products. Parent 5-hydroxy-substituted compounds **1a-1d** yielded exclusively "half-cage" dimers **3a-d** characteristic for 4-pyrone dimerization. 5-Methoxy-analogues **2a-2e** behave like typical stilbene structures and the mixture of tetrasubstituted cyclobutanes **4** and **5** accompanied with minor amount of phenanthrene-like compound **6** were the only isolable products of the irradiation**.** The structure elucidation of products is based on spectral data obtained from MS, IR, ^{1}H NMR and ^{13}C NMR spectra applying COSY, APT, HETCOR, HMBC and NOESY techniques.

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It is known that 4-pyrones and their derivatives are present in many natural materials and are found to be biologically active [1]. Some styryl-substituted 4-pyrones and chromones that have been found in various plants [1b,2], possess anticancer activity [1e,3]. Our continuing interest in the synthesis and photochemistry of 4-pyrones [4] as well as heteroaromatic stilbene-like compounds [5] have prompted us to study styryl-substituted 4-pyrones [6].

The photochemistry of 4-pyrones is well documented [7]. Similarly as with other enone systems [8], the main recognised processes are photodimerizations to "cage" compounds [9a], isomerizations to 2-pyrones [9d] and ring rearrangements to cyclopentadienone systems, often with the incorporation of a solvent molecule [7c]. The outcome of 4-pyrone photodimerizations as a consequence of a [2+2] photocycloaddition usually are the cyclobutane dimers [9a,9b,10] which often in subsequent reactions gave the cage-type compounds [9c,10c,11]. A particular interest deserve 4-pyrones with a side chain containing properly situated π-electronic systems [12,13b] in which cases the intramolecular photocycloadditions with significant regioselectivity, photoisomerizations and/or photodehydrocyclizations has been observed. The presence of β-hydroxy-group is highly in favour of photochemical ring contraction and many 4-pyrones with such substitution exhibit after photoexcitation the rearrangements to corresponding hydroxycyclopentenones [12,14].

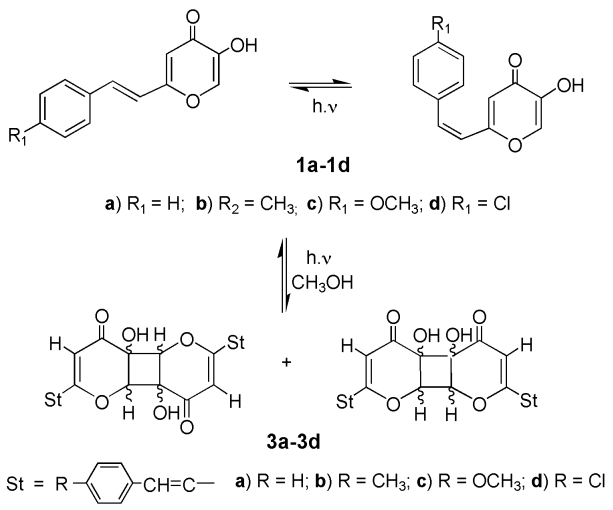
On the other hand the photochemical reactions of stilbene and stilbene-like compounds were subject of numerous studies [15]. Among these, various aromatic and heteroaromatic compounds bearing conjugated structures based on the bridging of heterocycles with alkenyl moieties were excited in the near ultraviolet in the crystalline morphologies and in solution [16]. The geometrical *E-Z* isomerization was often the dominant photochemical pathway in dilute solution [17], but photodehydrocyclization in polycondensed phenanthrene-like and helicene-type compounds are well known, too [18]. Another reaction pathway, most often found in concentrated media or more efficiently in crystalline state, is connected with [2+2] cyclodimerization through external unsaturation [19].

In continuation of our studies on 5-hydroxy-4-pyrones [4] we recently reported about the preparation of several substituted 2-styryl-4-pyrones [6]. Our interest for such arylethenylpyrones was founded by the fact that similar compounds isolated from plants and/or marine organisms attracted considerable interest for their unusual structure and concomitant biological activity [1-3]. The report about cyclobutane derivatives with 2-pyronyl substituent has appeared [1b] explaining the presence of such compounds in plants by light induced reactions. Besides, we believe that the reported suppression of melanine formation achieved with some skin-protection creams [20] containing β-hydroxystyrylpyrones as an additive, was in fact a consequence of a photochemical process.

A combination of two substructures like in 5-hydroxy- or 5-methoxy-2-styryl-4-pyrones may be useful example for the study and comparation of the photochemistry for both, 4-pyrone ring and stilbene-like system. The outcome of photochemical reaction, under the same reaction conditions applied both to parent 5-hydroxy-compounds (**1a-1d**) and to their methylated derivatives (**2a-2e**), was strikingly different.

With 5-hydroxy-2-styrylpyrones only "half-cage" dimers **3a-3d** were obtained as a result of [2+2] photodimerization caused by the pyrone excitation [9a] (Scheme 1).

Scheme 1



On the other hand such a photoreaction with 5-methoxy-derivatives **2a-2e** was substantially absent. The mixtures of cyclobutane dimers (**4a-4e** and/or **5a-5e**) formed, as the main products by ethene-ethene [2+2] photocycloaddition and minor quantities of electrocyclization products (**6a-6e**) (Scheme 2) were isolated.

The mechanistic path of studied photorections is believed to involve initial isomerization of the *trans*-isomer to the stationary state of *cis/trans* isomers. The photochemical experiments were performed under aerobic conditions with 6-9 x 10^{-3} *M* solutions in methanol, and the structures of products were determined spectroscopically.

A. Irradiation of 5-Hydroxy-2-styryl-4-pyrones and Structure Determination of Photoproducts.

A better insight in the photochemical transformations during prolonged irradiation has been achieved by the inspection of ^{1}H nmr spectra of evaporated aliquots taken from the reaction mixture within intervals stated. During irradiation of **1b** for 5-10 hours only the *E/Z* photoisomerization involving external double bond was observed. A photostationary state was achieved at 40/60 *E/Z* ratio. After prolonged irradiation for next 24 hours, appearance of several other compounds was observed. The reaction mixture was constituted of several individual components but similar Rf values and a very low solubility in most common organic solvents prevented us from separating them. We have continued with the irradiation for 24 hours more, until a single entity having elements of pyronic structure remained. From the crude reaction mixture containing a lot of tarry material column and thin layer chromatography have isolated the single photochemical product. The analogous treatment was applied to other studied compounds (**1a-1d**).

The mass spectra of the isolated products clearly pointed out the dimeric structure. The fragmentation pattern showed a high degree of structural similarities with starting compounds. Since three double bonds of **1a-1d** could be involved in [2+2] dimerization process, the numerous cyclobutane-type products could be formed. As for any 4-pyrone dimerization one could theoretically expect more isomers formed by either "head-to-tail" or "head-to-head" modes. The ^{1}H nmr spectra of obtained dimers pointed out the presence of unchanged *trans*-ethylenic moiety as two doublets at δ 7.25-7.41 ppm (d, 2H) and 7.49-7.70 ppm (d, 2H) with *J* = 16.0-16.6 Hz indicating that the principal structural changes must be located at 4-pyrone rings. From the simplicity of ^{1}H and ^{13}C nmr spectra a high symmetry of the products was evident. The presence of signals for protons C3 (and C3') at δ 6.32-6.42 ppm, being almost unchanged in comparison with the same protons in starting compounds, undoubtedly indicates that the reaction occurs at C5-C6 double bond and that the double bond C2-C3 conjugated with styryl group remained intact. The disappearance of hydroxylic protons of the starting materials at 8-9 ppm confirmed this conclusion. The dimerization through C5 and C6 atoms of pyrone rings confirms the ^{1}H nmr signal for protons at C6 (and C6') being shifted from δ 7.3-8.6 ppm (s, 1H) in **1a-1d** to δ ≈ 4.9 ppm (s, 2H) in isolated dimeric photoproduct. The same conclusion is reached by comparison of ^{13}C nmr signals for C5 (bearing the hydroxyl group) and C6 in **1a-1d** with those in corresponding isolated dimers showing significant shift from 146 and 135 ppm to 94 and 72 ppm respectively. The carbons C2 and C2', bearing the styryl group (δ 165 ppm), almost retained the value found in starting compounds (δ 161 ppm) showing that the partial structure at this point is not changed.

On that account a selection of "half-cage" dimers could be proposed *cis-syn-cis* (**A** and **C**) and *cis-anti-cis* (**B** and **D**), from either "head-to-head" or "head-to-tail" dimerization (Figure 1). Such a conclusion was supported by the analogy with the reported examples of 4-pyrone photodimerizations [9a,9b,9c,10b,10c]. Regarding the stereochemistry of formed "half-cage" cyclobutane ring the ^{1}H nmr data did not allow the isomers distinction [21]. Nevertheless, we ruled out the formation of "half-cage" structures **A** and **C** since *cis-syn-cis* isomers would be expected [10b] to react further toward the corresponding

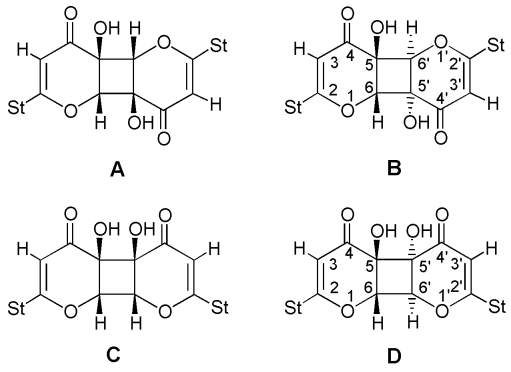


Figure 1

products with cage-like structures. No traces of such dimers with cage-like structure were detected even during prolonged irradiation, so the formation of solely *cis-anti-cis* (**B** or **D**) "half-cage" isomers was tentatively anticipated.

Due to symmetry reasons, even after very careful spectroscopic structure analyses using high resolution nmr correlations and NOE experiments we were not able to undoubtedly distinguish and assign the "head-to-tail" (**B**) and "head-to-head" (**D**) structure [22].

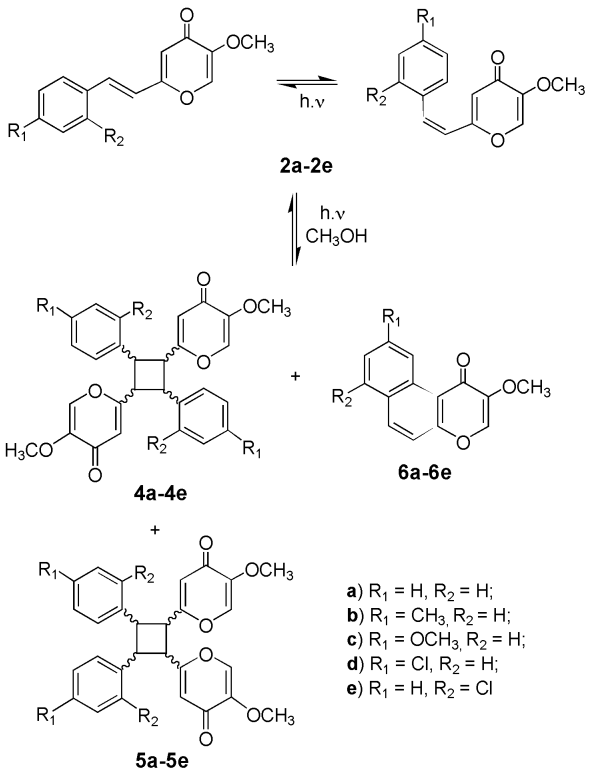
B. Irradiation of 5-Methoxy-2-styryl-4-pyrones and Structure Determination of Photoproducts.

The irradiation and isolation of products were identical or similar as in chapter A, but the formation of "half-cage" dimers was not detected. The only isolable products were tetrasubstituted cyclobutanes **4** and/or **5**, formed through the "ethene-ethene" dimerization, and phenanthrene-like photodehydrocyclization products *i.e.* benzo[*f*]chromones **6** (Scheme 2).

The structures of the products were determined spectroscopically. The MS spectra of compounds **4a-4d** and **5d**, **5e**, isolated by column chromatography from the posterior fractions, suggested the dimeric structures. From their ^{1}H nmr spectra it was obvious that the reaction took place at the ethylenic double bond. The signals for *trans* ethylenic double bond with the coupling constant of 16 Hz disappeared and two signals for four cyclobutane protons in a ratio 1:1 at 4.19-4.57 and 4.17-4.52 ppm appeared. All dimers are cyclobutane derivatives formed by a [2+2] cycloaddition reaction of two ethylenic bonds. Dimers **4a-4d** showed very small molecular ions M^+ and the base peaks at *m/z* $M^+/2$ so we assigned them as "head-to-tail" adducts. Compounds **5d** and **5e** are "head-to-head" dimers based on fragments *m/z* corresponding for 1,2-dipyroneethene and 1,2-diphenyl-ethene moiety characteristic for an unsymmetrical reversion, in addition to $M^+/2$ signals.

We could expect more isomers formed by *trans-trans*, *trans-cis*, and *cis-cis* dimerization in "head-to-head" and "head-to-tail" modes (Figure 2). The ^{1}H nmr spectra together with ^{13}C nmr data of all the isolated dimeric products pointed to the symmetrical cyclobutane structure. Based on NOE experiments, combined with the previously obtained data in our laboratory for stereochemical relationship of heterocyclic cyclobutane derivatives [23] the stereochemistry of compounds **4** and compounds **5** should correspond to structure **II** and **IV** in Figure 2, respectively.

Scheme 2



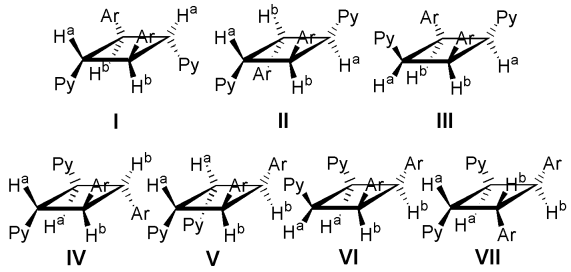


Figure 2

Table 1

Crystallographic data, structure solution and refinement of **4b**.

Molecular formula	$C_{30}H_{28}O_6$
M_r	484.52
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	9.709(5)
b / Å	16.880(5)
c / Å	15.189(5)
α / °	90.00
β / °	93.34(5)
γ / °	90.00
V / Å^3	2481.5(17)
Z	4
F (000)	1024
D_x / g cm^{-3}	1.295
μ (Mo-Kα) / mm^{-1}	0.09
Absorption correction	none
Total data collected	5326
Observed data [criterion]	557 [I > 2σ(I)]
R_{int}	0.2943
θ_{max} / °	26.29
R_1 [F_o>4σ(F_o)]	0.1262
Goodness of fit, S	0.866
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /eÅ^{-3}	0.33, -0.31

A final proof of the structure **II** depicted in Figure 2 was established by single crystal X-ray diffraction. The crystallographic data collected with an Enraf-Nonius CAD-4 diffractometer are summarised in Table 1.

Electron density maps unambiguously revealed the molecular structure [24]. The ORTEP view of the molecule is shown in Figure 3. The free rotations between pairs of bonds: C1-C5, C3-C21 and C2-C14, C4-C30 generate somewhat different orientations of chemically identical moieties. Therefore, the molecule exhibits *C*i symmetry.

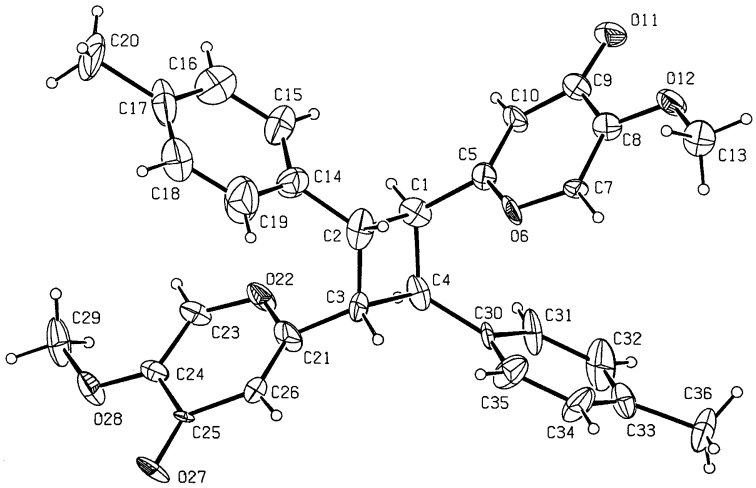
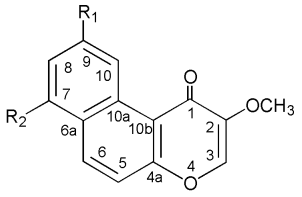


Figure 3

Molecular structure of **4b** (**II** in Figure 2) with thermal ellipsoids scaled at 30% probability level and the atom-numbering scheme.

The structures of the electrocyclization products *i.e.* benzo[*f*]chromones **6a**, **6d, 6e** (Figure 4) were determined spectroscopically as well. The MS spectra of compounds **6** showed molecular ions different for two units from the corresponding starting material, suggesting the formation of the electrocyclization structure.



6a-6e

Figure 4

From ^{1}H nmr spectra it was obvious that the signals of ethylenic double bond have disappeared and the new ones as a part of conjugated cyclic systems appeared (doublets near 7.7 ppm and 8.3 ppm with J = 9.06 Hz). The characteristic signals for hydrogens at C3 of the pyrone ring in the starting compounds **2** near 6.5 ppm disappeared too. That also happened with the aromatic proton in *o*-position of styryl group. ^{13}C NMR spectra confirmed the structure **6** by disappearance of a doublet at 113 ppm C3 in starting component, and the appearance of a singlet at 115 ppm. The signals for protons at C10 (Figure 4) in **6a**, **6d**, **6e** lie in a region deshielded by the carbonyl group that leads to their abnormally high δ values [9d] (≈ 10 ppm). The absence of cyclization *via* dehydrohalogenation in case of **2e** could be explained by steric factors (the system is out of planarity because of the repulsion with bulky chlorine atom).

From the obtained results we can conclude that the system after methylation of 5-hydroxy-group does not show the expected pyrone photochemistry but the preferred photochemical reaction is the [2+2] cyloaddition at the external ethylenic bond, characteristic for the stilbenes.

EXPERIMENTAL

Melting points were determined on an Original Kofler Mikroheitztisch apparatus (Reichardt, Wien) and were not corrected. Infrared spectra were taken in potassium bromide pellets with a Perkin-Elmer Model 297 instrument (vs = very strong, s = strong, m = medium, w = weak, vw = very weak). Ultraviolet spectra were recorded in methanol solution on a Hitachi-Perkin-Elmer Model 124 double beam spectrophotometer. Proton and ^{13}carbon nmr spectra were taken on a Varian GEMINI 300 spectrometer with tetramethylsilane as the internal standard in hexadeuteriodimethylsulfoxide solutions if not otherwise stated. Mass spectra were recorded on an Extrel FTMS 2001 DD spectrometer by direct insertion probe. X-Ray structure analysis was performed using an Enraf-Nonius CAD-4 diffractometer.

Irradiations were carried out in a quartz or pyrex vessel in a methanol solution (6-9 x 10^{-3} *M*). A "Rayonet" RMR 400 or "Rayonet" RPR 100 photochemical reactors equipped with RPR 300 nm lamps were used. Alternatively, a water cooled quartz or pyrex immersion well fitted with 400 w high pressure mercury arc lamp was used. Photochemical reactions were carried out in aerobic conditions under bubbling of an air stream through the irradiated solution. If not stated otherwise, the progress of the photochemical reaction was monitored by ultraviolet spectra and by thin layer chromatography on the "Merck" silica gel 60 F_{254} alufoils. Standard column chromatography was carried out on the "Kemika" silica gel 60-230 mesh ASTM. Solvents ("Kemika") were purified by distillation. Starting compounds (mainly *trans* isomer according to the melting point) were prepared by a Wittig reaction from (5-hydroxy- or 5-methoxy-4-pyron-2-yl)methyltriphenylphosphonium chloride and corresponding aldehyde as described [6].

Irradiation of 2-(2-Phenylethenyl)-5-hydroxy-4*H*-pyran-4-one (**1a**).

The solution of **1a** (75 mg, 0.35 mmoles) in methanol (15 ml) was irradiated with RPR 300 nm lamps for 60 hours in a quartz tube. The solvent was removed under reduced pressure. The dark oily residue crystallized upon standing at room temperature. The crystalline residue was washed with chloroform/methanol 2:1 and recrystallized from methanol to give **3a** (32 mg, 41%). The

combined filtrates were evaporated and chromatographed on silica gel column using chloroform/methanol 20:1 as eluent. The starting material (15 mg, 20%), and an additional quantity of **3a** (5 mg, 6.4%) was obtained. The rest was tarry material that remained on the column.

4a,4b,8a,8b-Tetrahydro-4a,8a-dihydroxy-2,6-bis(phenylethenyl)cyclobuta[1,2-*b*:3,4-*b'*]dipyran-4,8-dione (**3a**).

This compound (37 mg, 47.4%) melted at mp 215-217°; uv: (λ_{max}/nm) 330, 241, 234; ir: 3380 (s), 3080 (vw) 2910 (vw), 1690 (vs), 1610 (vs), 1580 (s), 1450 (w), 1390 (w), 1125 (w), 1100 (w), 1030 (s), 965 (s), 760 (s), 690 (s) cm^{-1}; ^1H nmr: δ 7.35-7.75 (m, 14H), 6.42 (s, 2H), 4.91 (s, 2H); ^{13}C nmr: δ 199.2 (s), 165.6 (s), 140,8 (d), 135.7 (s), 130.4 (d), 129.4 (d), 129.1 (d), 128.3 (d), 122.3 (d), 94.8 (s), 72.0 (d).

Anal. Calcd. for $C_{26}H_{20}O_6 \cdot H_2O$ (446.45): C, 69.95; H, 4.97. Found: C, 70.14; H, 4.80.

Irradiation of 2-[2-(4-Methylphenyl)ethenyl]-5-hydroxy-4*H*-pyran-4-one (**1b**).

The methanolic solution of **1b** (500 mg, 2.19 mmoles in 200 ml) was divided in two portions which were simultaneously irradiated in (a) quartz and (b) pyrex tube with the light from a water cooled high pressure 400 w mercury arc lamp. After 50 hours the solvent was evaporated. The progress of irradiations were followed by uv, tlc and ^1H nmr techniques and the results were identical. Both irradiated solutions were combined and evaporated. The residue was triturated with methanol (8 ml). The precipitate was isolated by filtration and recrystallized from diethylacetate/methanol 4:1 to give **3b** (149 mg, 29%). The methanolic solution after precipitation was evaporated and chromatographed on silica gel column using chloroform/methanol 20:1 as the eluent. From the faster moving fractions 150 mg (30%) of **1b** was recovered and the later fractions afforded the additional crop of **3b** (57 mg, 11%). The combined crops of crude **3b** were recrystallized from ethylacetate/methanol 1:2 to give 186 mg of the pure compound.

4a,4b,8a,8b-Tetrahydro-4a,8a-dihydroxy-2,6-bis[(4-methylphenyl)ethenyl]cyclobuta[1,2-*b*:3,4-*b'*]dipyran-4,8-dione (**3b**).

Microcrystalline colourless **3b** (186 mg, 40%) melted at mp 236-238°; uv: (λ_{max}/nm) 342, 246, 238; ir: 3325 (vs), 2900 (vw), 1690 (vs), 1570 (vs), 1320 (s), 1220 (w), 1120 (vs), 980 (w), 890 (w), 860 (w), 670 (w) cm^{-1}; ^1H nmr: δ 7.70 (d, 2H, *J* = 15.96 Hz), 7.65 (d, 4H, *J* = 8.05 Hz), 7.33 (d, 2H, *J* = 16.05 Hz), 7.32 (d, 4H, *J* = 8.1 Hz) 6.32 (s, 2H), 4.90 (s, 2H), 2.35 (s, 6H); ^{13}C nmr: δ 198.1 (s), 165.1 (s), 140.1 (d), 139.7 (s), 132.6 (s), 129.3 (d), 127.9 (d), 127.9 (d), 120.9 (d), 94.4 (s), 71.9 (d); ms: m/z (relative intensity) 228 (M^+/2, <1), 214 (14), 196 (6), 157 (20), 129 (100), 115 (17), 102 (9), 91 (9), 84 (6), 77 (14), 57 (10).

Anal. Calcd. for $C_{28}H_{24}O_6 \cdot H_2O$ (474.51): C, 70.87; H, 5.52. Found: C, 70.90; H, 5.85.

Irradiation of 2-[2-(4-Methoxyphenyl)ethenyl]-5-hydroxy-4*H*-pyran-4-one (**1c**).

A methanolic solution of **1c** (250 mg, 1.02 mmoles in 125 ml) was irradiated with RPR 300 nm lamps in a quartz tube for 60 hours. The solvent was evaporated. On addition of chloroform (5 ml) the reaction mixture solidified. The collected solid was isolated by filtration and recrystallized from methanol to give **3c** (112 mg, 44%). Combined mother liquors were chromatographed using silica gel column eluted with chloroform/ methanol 20:1 to give 50 mg (20%) of starting compound **1c** and an additional crop of compound **3c** (26 mg, 10%).

4a,4b,8a,8b-Tetrahydro-4a,8a-dihydroxy-2,6-bis[(4-methoxyphenyl)ethenyl]cyclobuta[1,2-*b*:3,4-*b'*]dipyran-4,8-dione (**3c**).

Microcrystalline, pale-beige **3c** (138 mg, 54%) melted at 235-237°; uv: (λ_{max}/nm) 360, 242, 225; ir: 3360 (s), 1690 (vs), 1610 (w), 1590 (vs), 1555 (vs), 1320 (w), 1250 (vs), 1170 (s), 1120 (s), 950 (w), 880 (w) cm^{-1}; ^1H nmr: δ 7.72 (d, 4H, *J* = 8.38 Hz), 7.49 (d, 2H, *J* = 16.11 Hz), 7.25 (d, 2H, *J* = 16.11 Hz), 7.08 (d, 4H, *J* = 8.38 Hz), 6.32 (s. 2H), 4.88 (s, 2H), 3.84 (s, 6H); ^{13}C nmr: δ 196.0 (s), 166.0 (s), 161.3 (s), 140.7 (d), 130.1 (d), 128.3 (s), 127.8 (d), 119.9 (d), 114.8 (d), 94.9 (s), 72.0 (d), 55.5 (q); ms: m/z (relative intensity) 489 (M^+, 8), 456 (31), 391 (38), 307 (78), 289 (36), 256 (38), 244 (M^+/2, 6), 154 (100), 136 (68), 120 (13), 107 (24), 91 (37), 65 (9).

Anal. Calcd. for $C_{28}H_{24}O_8 \cdot H_2O$ (506.50): C, 66.40; H, 5.17. Found: C, 66.58; H, 4.96.

Irradiation of 2-[2-(4-Chlorophenyl)ethenyl]-5-hydroxy-4*H*-pyran-4-one (**1d**).

The solution of **1d** (250 mg, 1.0 mmol) in methanol (125 ml) was irradiated with 16 RPR 300 nm lamps in a quartz tube for 56 hours. On evaporation *in vacuo* the dark-reddish oil was chromatographed on silica gel column using chloroform/methanol 20:1 as eluent. From faster moving fractions 29 mg (12%) of starting **1d** was recuperated. Slower moving fractions enriched in compound **3d** were combined. Further purification by repeated column chromatography was not successful but the pure **3d** (98 mg, 39%) was obtained using the preparative thin layer chromatography on silica gel with chloroform/methanol 4:1 as the eluent and recrystallization from methanol.

4a,4b,8a,8b-Tetrahydro-4a,8a-dihydroxy-2,6-bis[(4-chlorophenyl)ethenyl]cyclobuta[1,2-*b*:3,4-*b'*]dipyran-4,8-dione (**3d**).

The colourless, microcrystalline **3d** (98 mg, 39%) melted at 228-230°; uv: (λ_{max}/nm) 335, 235; ir: 3340 (s), 1700 (vs), 1615 (vs), 1580 (vs), 1490 (s), 1315 (s), 1090 (s), 970 (w), 860 (w) cm^{-1}; ^1H nmr: δ 7.76 (d, 4H, *J* = 7.32 Hz), 7.57 (d, 4H, *J* = 7.32 Hz), 7.52 (d, 2H, *J* = 16.65 Hz), 7.46 (d, 2H, *J* = 16.65 Hz), 6.42 (s, 2H), 4.90 (s, 2H); ^{13}C nmr: δ 199.2 (s), 165.3 (s), 139.4 (d), 134.8 (s), 134.7 (s), 129.9(d), 129.4 (d), 127.2 (d), 123.0 (d), 94.8 (s), 72 (d); ms: m/z (relative intensity) 496 (M^+,<1), 355 (7), 354 (29), 337 (5), 274 (6), 250 (3), 248 (1/2 M^+/2,12), 222 (11), 220 (40), 194 (7), 192 (29), 165 (17), 163 (47), 137 (12), 135 (14), 129 (100), 128 (51), 111 (21), 99 (13), 97 (20), 85 (23), 71 (15), 57 (12).

Anal. Calcd. for $C_{26}H_{18}Cl_2O_6$ (497.33): C, 62.79; H, 3.65. Found: C, 62.49; H, 3.76.

Irradiation of 2-(2-Phenylethenyl)-5-methoxy-4*H*-pyran-4-one (**2a**).

A solution of **2a** (730 mg, 3.19 mmoles) in 350 ml of methanol after 15 hours of irradiation was evaporated under reduced pressure and the reaction mixture eluted with petroleum ether/acetone (5:1) on a column of silica gel to give (29 mg, 4%) of electrocyclization product **6a**. Eluting with progressively more polar petroleum ether/acetone solution (from 5:1 to finally 1:1) produced a mixture of dimeric products (221 mg, 31%) as the later fractions (uv spectra $\lambda_{max} \approx 265$ nm) from which dimer **4a** was isolated. The former (middle fractions) being unreacted starting material (247 mg, 34%). The last fraction eluted with methanol

gave tarry material (106 mg, 22%). After repeated column chromatography and recrystallization from ethylacetate/methanol the dimer **4a** (51 mg, 23%) was obtained. Some minor quantities of unidentified dimeric products (19 mg, 8.6%) were also obtained.

2-Methoxy-1*H*-naphtho[2,1-*b*]pyran-1-one (**6a**).

Colourless crystals of this compound (29 mg, 4%) melted at mp 212-214°; uv: (λ_{max}/nm) 310, 282, 250, 230; ir: 3350 (w), 2990 (w), 1645 (vs), 1639, vs, 1590 (s), 1570 (s), 1450 (s), 1370 (s), 1310 (s), 1250 (s), 1240 (s), 1190 (s), 1075 (s) 1000 (s), 950 (s), 880 (s), 820 (s), 760 (s), 715 (s); ^{1}H nmr (deuteriochloroform): δ 9.95 (d, 1H, *J* = 8.52 Hz, H-10), 8.39 (s, 1H, H-3), 8.27 (d, 1H, *J* = 9.06 Hz, H-5), 8.08 (d, 1H, *J* = 8.01 Hz, H-7), 7.78 (dd, 1H, *J* = 8.52, 7.08 Hz, H-9), 7.69 (d, 1H, *J* = 9.06 Hz, H-6), 7.68 (dd, 1H, *J* = 8.01, 7.08 Hz, H-8) 3.78 (s, 3H, OCH_3); ^{13}C nmr (deuteriochloroform): δ 173.4 (s, C-1), 156.4 (s, C-4a), 146.2 (s, C-2), 138.1 (d, C-3), 135.6 (d, C-6), 130.1 (s) and 129.9 (s) for C-6a and C-10a, 129.2 (d), 128.7 (d), 126.6 (d), 126.0 (d) for C-7, C-8, C-9 and C-10, 118.2 (d, C-5), 115.9 (s, C-10b), 56.8 (q, OCH_3).

Anal. Calcd for $C_{14}H_{10}O_3$ (226.23): C, 74.33; H, 4.46. Found: C, 74.48; H, 4.52.

r-1,*t*-3-Di(5-methoxy-4-pyron-2-yl)-*c*-2,*t*-4-diphenylcyclobutane [*r*-*ctt* htt dimer] [25] (**4a**).

The colourless crystals of **4a** (51 mg, 23%) melted at mp 217-218°; uv: (λ_{max}/nm) 266; ir: 1645 cm^{-1}($\nu_{C=O}$); ^{1}H nmr (deuteriochloroform): δ 7.63 (s, 2H, pyrone H-6), 7.09-7.38 (m, 10H, Ar-H), 6.26 (s, 2H, pyrone H-3), 4.38 (m, 2H) and 4.28 (m, 2H) for cyclobutane H^a and H^b respectively; 3.63 (s, 6H, OCH_3); ms: m/z (relative intensity) 279 (18), 249 (43), 235 (100), 227 (M^+/2, 93), 197 (15), 183 (14), 169 (18), 155 (18), 141 (19), 127 (26), 113 (32), 99 (33), 85 (40), 71 (28), 57 (20).

Anal. Calcd for $C_{28}H_{24}O_6$ (456.49): C, 73.67; H, 5.29. Found: C, 73.49; H, 5.14.

Irradiation of 2-[2-(4-Methylphenyl)ethenyl]-5-methoxy-4*H*-pyran-4-one (**2b**).

After 9 hours of irradiation of **2b** (500 mg, 2.06 mmoles) in 300ml methanol and evaporation of the reaction mixture (a yellow-red oil) was eluted with petroleum ether/acetone on a column of silica gel to give several different fractions. The first fractions were small quantities of unidentified product (9 mg, 1.8%), the middle fractions were the mixture of unreacted starting compound **2b** (265 mg, 53%) and the later fractions the mixture of dimeric products (185 mg, 37%). Tarry material remained on the column. By repeated column chromatography (ethylacetate/petroleum ether 5:1) from the mixture of dimeric isomers only one dimer was isolated in a greater extent (**4b**, 91 mg, 49%).

Anal. Calcd. for dimeric mixture $C_{30}H_{28}O_6$ (484.54): C, 74.37; H, 5.82. Found: C, 74.56, H, 5.97.

r-1,*t*-3-Di(5-methoxy-4-pyron-2-yl)-*c*-2,*t*-4-di(4-methylphenyl)-cyclobutane [*r*-*ctt* htt dimer] [25] (**4b**).

Colourless crystals of this compound (91 mg, 49%) melted at mp 215-216°; uv: (λ_{max}/nm) 265; ir: 3090 (w), 2900 (w), 1640 (vs), 1610 (vs), 1585 (vs), 1510 (s), 1440 (s), 1410 (s), 1380 (s), 1240 (vs), 1230 (vs), 1189 (vs), 1150 (s), 1000 (vs), 950 (s), 870 (s), 800 (vs); ^{1}H nmr (deuteriochloroform): δ 7.99 (s, 2H, pyrone H-6), 7.39 (d, 4H, *J* = 8.49 Hz,), 7.24 (d, 4H, *J* = 8.49 Hz), 6.37 (s, 2H, pyrone H-3), 4.51 (m, 2H), 4.47 (m, 2H), 3.64 (s, 6H, OCH_3), 2.35 (s, 6H, CH_3); ^{13}C nmr (deuteriochloroform): δ 173.7 (s), 165.8 (s), 148.4 (s), 137.8 (s), 137.1 (d), 134.1 (s), 129.4 (d) and 126.9 (d) for C-2 of two pyrone rings, 114.2 (d, pyrone C-3), 56.3 (q, OCH_3), 45.4 (d) and 43.6 (d) for cyclobutane carbons, 21.1 (q, CH_3); ms: m/z (relative intensity) 485 (MH^+, 34), 484 (9), 242 (M^+/2, 100), 196 (38), 159 (8), 128 (7), 105 (6).

Irradiation of 2-[2-(4-Methoxyphenyl)ethenyl]-5-methoxy-4*H*-pyran-4-one (**2c**).

A solution of **2c** (500 mg, 1.94 mmoles) in 300 ml methanol after irradiation (13 hours) and evaporation of the solvent was fractionated by column chromatography on silica gel into several fractions as follows: a small quantity (10 mg, 2%) of unidentified material (uv: λ_{max} 220, 260, 345 nm) followed by the mixture of starting compound (131 mg, 26%) and the mixture of dimers (231 mg, 46%). The last fractions eluted with methanol were some tarry material (46 mg, 9.2%). After second column chromatography of the dimeric mixture and recrystallization from ethylacetate/methanol, a dimer **4c** (116 mg, 50%) was isolated and the rest was a mixture of other unidentified dimers (39 mg, 8%).

Anal. Calcd. for dimeric mixture $C_{30}H_{28}O_8$ (516.54): C, 69.76; H, 5.46. Found; C, 69.57; H, 5.31.

r-1,*t*-3-Di(5-methoxy-4-pyron-2-yl)-*c*-2,*t*-4-di(4-methoxyphenyl)cyclobutane [*r*-*ctt* htt dimer] [25](**4c**).

This compound (116 mg, 50%), colourless crystals, melted at mp 178-179°; uv: (λ_{max}/nm) 266; ir: 3050 (w), 2900 (w), 2800 (w), 1640 (vs), 1630 (s), 1580 (s), 1500 (s), 1450 (s), 1410 (s), 1260 (vs), 1220 (vs), 1170 (s), 1020 (s), 1000 (s), 980 (w), 920 (w), 820 (s), 800 (s); ^{1}H nmr (deuteriochloroform): δ 7.32 (s, 2H, pyrone H-6), 7.11 (d, 4H, *J* = 8.42 Hz), 6,81 (d, 4H, *J* = 8.42 Hz), 6.23 (s, 2H, pyrone H-3), 4.33 (m, 2H, H^a), 4.17 (dd, 2H, J = 8.65, 8.56 Hz, H^b), 3.77 (s, 6H, aryl OCH_3), 3.54 (s, 6H, pyrone OCH_3); ^{13}C nmr (deuteriochloroform): δ 173.5 (s), 165.7 (s), 158.6 (s), 148.2 (s), 137.2 (d), 128.9 (s), 128.0 (d), 114.0 (d), 56.3 (q, pyrone OCH_3), 55.1 (q, aryl OCH_3), 45.6 (d), 43.1 (d); ms: m/z (relative intensity) 516 (M^+, 1), 259 (M^+/2, 100), 154 (51), 136 (36), 121 (16), 91(22).

Irradiation of 2-[2-(4-Chlorophenyl)ethenyl]-5-methoxy-4*H*-pyran-4-one (**2d**).

After 15 hours of irradiation of **2d** (700 mg, 2.66 mmoles) in 300 ml methanol, and column chromatography on silica gel by elution with ether/acetone 10:1, the photodehydrocyclization product **6d** (57 mg, 8%) and two dimers **4d** and **5d** (216 mg, 31%) were obtained. The starting material **2d** (298 mg, 42.5%) was also recovered. The tarry material (108 mg, 15.43%) was obtained by elution with methanol. The preparative thin layer chromatography using chloroform/petroleum ether 9:1 gives pure isomers **4d** and **5d** beside the minor quantity of some unidentified dimers.

Anal. Calcd. for the mixture of dimeric products $C_{28}H_{22}Cl_2O_6$ (525.38): C, 64.01; H, 4.22; Cl, 13.50. Found: C, 63.81; H, 4.02; Cl, 13.35.

9-Chloro-2-methoxy-1*H*-naphtho[2,1-*b*]pyran-1-one (**6d**).

Colourless crystals of **6d** (21 mg, 3%) melted at mp 167-169°; uv: (λ_{max}/nm) 310, 250, 220; ir: 1645 cm^{-1}($\nu_{C=O}$); ^{1}H nmr: δ 10.01 (d, 1H, *J* = 2.19 Hz), 8.43 (s, 1H), 8.32 (d, 1H, *J* = 9.06 Hz), 8.14 (d, 1H, *J* = 8.57 Hz), 7.75 (d, 1H, *J* = 9.06 Hz), 7.73 (d, 1H, *J* = 8.57, 2.19 Hz), 3.79 (s, 3H, OCH_3); ^{13}C nmr: δ 173.8 (s),

157.4 (s), 148.1 (s), 139.8 (d), 134.3 (d), 134.1 (s), 132.2 (s), 128.6 (d), 128.5 (d), 127.9 (s), 125.2 (d), 117.6 (d), 114.8 (s), 56.1 (q, OCH_3); ms: m/z (relative intensity) 263 (27), 262 (30), 261 (M^+, 100), 225 (67), 195 (50), 186 (27), 139 (76), 126 (17).

Anal. Calcd for $C_{14}H_9ClO_3$ (260.67): C, 64.51; H, 3.48; Cl, 13.60. Found: C, 64.32; H, 3.36; Cl, 13.46.

r-1,*t*-3-Di(5-methoxy-4-pyron-2-yl)-*c*-2,*t*-4-di(4-chlorophenyl)-cyclobutane [*r-ctt* htt dimer] [25] (**4d**).

Colourless crystals (47 mg, 21%) melted at mp 105-107°; uv: (λ_{max}/nm) 266; ir: 3080 (w), 2900 (w), 1645 (vs), 1610 (s), 1585 (w), 1490 (s), 1415 (s), 1240 (vs), 1235 (s), 1180 (s), 1090 (s), 1010 (s), 820 (s), 720 (w); ^{1}H nmr (deuteriochloroform): δ 7.87 (s, 2H), 7.31 (m, 8H), 6.29 (s, 2H), 4.57 (m, 2H), 4.52 (m, 2H), 3.53 (s, 6H, OCH_3); ^{13}C nmr (deuteriochloroform): δ 172.5 (s), 165.4 (s), 147.7 (s), 139.2 (d), 137.2 (s), 131.6 (s), 129.5 (d), 128.3 (d), 113.8 (d), 56.2 (q, OCH_3), 44. 2 (d), 42.2 (d); ms: m/z (relative intensity) 264 (37), 262 (100, M^+/2), 233 (12), 227 (5) 217 (3), 215 (7), 191 (7), 181 (10), 164 (11), 162 (17), 153 (8), (139), 129(18), 127 (34), 115 (6), 99 (8), 77 (7), 69 (19), 57 (11).

r-1,*t*-2-Di(5-methoxy-4-pyron-2-yl)-*c*-3,*t*-4-di(4-chlorophenyl)-cyclobutane [*r-tct* hth dimer] [25] (**5d**).

This compound (36 mg, 16.4%) melted at mp 161-162º; uv: (λ_{max}/nm) 268; ir: 3080 (w), 2920 (w), 1645 (vs), 1610 (w), 1590 (s), 1490 (s), 1450 (w), 1420 (w), 1225 (vs), 1190 (s), 1010 (w), 935 (s), 835 (s), 730 (w); ^{1}H nmr (deuteriochloroform): δ 8.04 (s, 2H), 7.24 (d, 4H, *J* = 8.49 Hz), 7.19 (d, 4H, *J* = 8.49 Hz), 6.46 (s, 2H), 4.47 (s, 2H), 4.45 (s, 2H), 3.60 (s, 6H, OCH_3); ^{13}C nmr (deuteriochloroform): δ 172.8 (s), 165.6 (s), 148.1 (s), 139,6 (d). 137.5 (s), 131.4 (s), 130.1 (d), 128.2 (d), 113.3 (d), 56.3 (q, OCH_3), 43.6 (d), 42.6 (d); ms: m/z (relative intensity) 276 (Py-CH=CH-Py, 26), 264 (42), 262 (M^+/2, 100), 248 (Ar-CH=CH-Ar, 13), 131 (7).

Irradiation of 2-[2-(2-Chlorophenyl)ethenyl]-5-methoxy-4-*H*-pyran-4-one (**2e**).

The solution of **2e** (700 mg, 2.66 mmoles) in 300 ml of methanol was irradiated during 15 hours. The solvent was evaporated and the reaction mixture fractionated on a silica gel column with petroleum ether/acetone (5:1). The polarity of solvent was graduated slowly (to 1:1). The first several fractions contained small quantities of cyclization product (67 mg, 9%) from which 2.4% of colourless crystals **6**e were obtained (recrystallization from ethylacetate/petroleum ether). The middle fractions were starting compound (368 mg, 52%) and the last fractions the mixture of dimers (214 mg, 31%). The tarry material remained on the column. The pure dimer **5e** was isolated by preparative thin layer chromatography on silica gel plates using chloroform/petroleum ether (9:1) as eluent.

7-Chloro-2-methoxy-1*H*-naphtho[2,1-*b*]pyran-1-one (**6e**).

Colourless crystals of **6e** (17 mg, 2.4%) melted at mp 164-166°; uv: (λ_{max}/nm) 312, 260, 252; ir: 1640 cm^{-1} ($\nu_{C=O}$); ^{1}H nmr (deuteriochloroform): δ 10.2 (d, 1H), 8.60 (d, 1H, *J* = 8.59 Hz), 7.75 (s, 1H), 7.70 (m, 2H), 7.62 (d, 1H, *J* = 8.59 Hz), 3.91 (s, 3H, OCH_3); ^{13}C nmr (deuteriochloroform): δ 172.6 (s), 157.1 (s), 146.7 (s), 138,2 (d), 134.8 (d), 131.7 (s), 130,1 (s), 128.5 (d), 128.2 (s) 126.3 (d), 124.1 (d), 117.9 (d), 115.1 (s), 56.2 (q, OCH_3); ms: m/z (relative intensity) 262 (12), 261 (21), 260 (M^+, 97), 245 (14), 244 (26), 232 (17), 226 (15), 225 (20), 179 (29), 169 (15), 141 (26), 127 (25), 125 (43), 113 (47), 111 (62), 71 (100).

Anal. Calcd. for $C_{14}H_9ClO_3$ (260.67): C, 64.51; H, 3.48; Cl, 13.60. Found: C, 64.67; H, 3.59; Cl, 13.82.

r-1,*t*-2-Di(5-methoxy-4-pyron-2-yl)-*c*-3,*t*-4-di(2-chlorophenyl)-cyclobutane [*r-tct* hth dimer] [25] (**5e**).

Colourless crystals (98 mg, 46%) melted at mp 185-186°; uv: (λ_{max}/nm) 268; ir: 3090 (w), 2960 (w), 1640 (vs), 1610 (w), 1590 (s), 1470 (s), 1430 (w), 1410 (w), 1230 (vs), 1180 (s), 1150 (w), 1090 (s), 990 (s), 940 (w), 910 (w), 810 (s), 750 (w), 720 (w); ^{1}H nmr (deuteriochloroform): δ 7.86 (s, 2H), 7.66 (d, 2H *J* = 7.60 Hz), 7.44 (dd, 2H, *J* = 7.45, 7.60 Hz), 7.40 (d, 2H *J* = 7.47 Hz), 7.30 (dd, 2H, *J* = 7.47, 7.45 Hz), 6.28 (s, 2H), 4.69 (s, 4H), 3.52 (q, 6H, OCH_3); ^{13}C nmr (deuteriochloroform): δ 172.3 (s), 164.7 (s), 147.8 (s), 139.1 (d), 134.8 (s), 133.4 (s), 129.4 (d), 129.1 (d), 128.2 (d), 127.4 (d), 113.9 (d), 56.1 (q, OCH_3), 42.5 (d), 41.1 (d); ms: m/z (relative intensity) 529 (12), 527 (62), 525 (100, M^+), 275 (Py-CH=CH-Py, 7), 265 (17), 263 (M^+/2, 61), 249 (Ar-CH=CH-Ar, 6), 227 (8), 181(8), 152 (7), 128 (6), 61(4).

Anal. Calcd. for $C_{28}H_{22}Cl_2O_6$ (525.38): C, 64.01; H, 4.22; Cl, 13.50. Found: C, 64.21; H, 4.34; Cl, 13.68.

X-ray Crystallographic Analysis of **4c**.

Suitable single crystals were obtained by slow evaporation from ethylacetate at room temperature. Table 1 summarizes crystal data, experimental details of data collection and refinement. Intensities were measured on an Enraf-Nonius CAD-4 diffractometer, with graphite monochromated MoK_α radiation, wavelength 0.71083 Å, using $\omega/2\theta$ scan technique. The data were corrected for Lorentz and polarization effects [26]. Structure was solved using the package SIR97 [27] and refined by the package SHELXL97 [28]. The crystal quality was rather poor and in spite of numerous crystallization attempts a perfect quality crystals were not obtained. Diffracting power of a crystal was rather limited and the number of the observed intensities is too low. Therefore the final *R* [for $F_o > 4\sigma(F_o)$] is 0.1262. However, electron density maps unambiguously revealed the molecular structure of the compound. Molecular geometry calculations were performed by PLATON98 [29]. Plot of the molecule with thermal ellipsoids scaled at the probability level 30% was prepared by ORTEP [30]. Atomic scattering factors were those included in SHELXL97. The H-atom coordinates were calculated geometrically and refined using the SHELX97 riding model.

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REFERENCES AND NOTES

Author to be contacted concerning X-ray structure determinations.

[1a] See *e. g.*: [a] S. Yamamura and S. Nishiyama, *Bull. Chem. Soc. Jpn.*, **70**, 2025 (1997); [b] M. H. Rossi, M. Yoshida and G. S. Maia, *Phytochemistry*, **45**, 1263 (1997); [c] W. A. Price, A. M. S. Silva and J. A. Cavaleiro, *Heterocycles*, **36**, 2601 (1993); [d] A. J. Blackman, J. B. Bremner, A. M. C. Paano, J. H. Skerrat and M. L. Swann, *Aust. J. Chem.*, **43**, 1133 (1990); [e] W. H. Gerwick, *J. Nat. Prod.*, **52**, 252 (1989); [f] W.

H. Gerwick, A. Lopez, G. D. Van Duyne, J. Clardy, W. Ortiz and A. Baez, *Tetrahedron Lett.*, **27**, 1979 (1996).

[2] M. Mimura and Y. Torri, *Jpn. Kokai Tokkyo Koho,* JP 63, 275, 577 (88, 275, 577) (Cl. C07D309/40), 14 Nov. **1988**, Appl., 87/110, 280 (06 May 1987); cit. *Chem. Abstracts*, **110**, P 236968n (1989).

[3] J. D. Brion, G. Le Baut, F. Zammattio, A. Pierre, G. Atassi, and L. Belachmi, *Eur. Pat. Appl*., EP 454,587 (1991*); Chem. Abstr*. 1992, **116**, 106092 k.

[4a] M. J. Herak, B. Tamhina, and K. Jakopčić, *J. Inorg. Nucl. Chem.,* 1973, **35**, 1665; [b] B. Tamhina, K. Jakopčić, F. Zorko, and M. J. Herak, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1855; [c] K. Jakopčić, B. Tamhina, F. Zorko, and M. J. Herak, *J. Inorg. Nucl.Chem.*, 1977, **39**, 1201; [d] V. Vojković and B. Tamhina, *Solvent Extr. Ion Exch.,* 1987, **5**, 245 and preceding papers; [e] Z. Stiplošek, M. Šindler-Kulyk, K. Jakopčić, Z. Meić, and D.Vikić-Topić, *J. Heterocyclic Chem.,* 1989, **26**, 1707; [f] K. Jakopčić, J. Kojić, Z. Orhanović, Z. Stiplošek, A. Nagl, and A. Hergold, *J. Heterocyclic Chem.,* 1992, **29**, 107; [g] K. Jakopčić, M. Mintas, and I. Isufi, *J. Heterocyclic Chem.,* 1993, **30**, 429; [h] M. Kožul, Z. Stiplošek, J. Kojić, Z. Orhanović, and K. Jakopčić, *Synth. Commun.*, 1997, **27**, 3711; [i] M. Kožul, Z. Stiplošek, Z. Orhanović and K. Jakopčić, *J. Heterocyclic Chem.*, **36**, 493 (1999) and references cited therein.

[5a] M. Šindler-Kulyk, I. Škorić, S. Tomšić, Ž. Marinić, and D. Mrvoš-Sermek, *Heterocycles*, 1999, **51**, 1355; [b] M. Šindler-Kulyk, Z. Stiplošek, D. Vojnović, B. Metelko, and Ž. Marinić, *Heterocycles*, 1991, **32**, 2357; [c] M. Šindler-Kulyk, Z. Stiplošek, and B. Metelko, *Croat. Chem. Acta***,** 1989, **62**, 81.

[6] Z. Stiplošek, M. Šindler--Kulyk, and K. Jakopčić *Org. Preparations and Procedures Int.*, 1999, **31**, 341.

[7a] See *e. g.*: G. P. Ellis, Comprehensive Heterocyclic Chemistry, Vol **3**, Part **2b**, A. R. Katritzky and C. W. Rees, eds, Pergamon Press Co, Oxford, 1984, p. 693; [b] A. R. Katritzky and N. Dennis, *Chem. Rev*, **89,** 827 (1998); [c] J. W. Pawlik, CRC Handbook of Organic Photochemistry and Photobiology, W. M. Horspool and Pill-Soon Song, eds, CRC Press, Boca Raton, 1995, p. 237.

[8] To illustrate tremendous progress achieved in this field see *e. g.* J.-P. Pete in Advances in Photochemistry, Vol. **21**, D. C. Neckers, D. H. Volman and G. von Bünau, editors, Willey Interscience, New York (1997) p. 135.

[9a] P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.,* **85**, 2956 (1963); [b] P. Yates, E. S. Hand, P. Singh, S. K. Roy and I. W. J. Still, *J. Org. Chem.*, **34**, 4046 (1969); [c] D. J. MacGregor, *Mol. Photochem.,* **6** (1), 101 (1974); [d] N. Ishibe, M. Sunami and M. Odani, *J. Am. Chem. Soc.*, **95**, 463 (1973); [e] J. W. Pavlik, E. B. Keil and E. L. Sullivan, *J. Heterocyclic Chem.,* **29**, 1829 (1992).

[10a] D. H. R. Barton and L. A. Hulshof, *J. Chem. Soc. (Perkin I)*, 1103 (1977); [b] K. A. Kumar and G. Srimannarayama, *Indian J. Chem.*, **16B**, 615 (1980); [c] F. G. West C. Hartke-Karger, D. J. Koch, S. E. Kuehn and A. M. Arif, *J. Org. Chem.*, **58**, 6795 (1993).

[11a] F. G. West, P. V. Fisher and C. A. Willoughby, *J. Org. Chem.*, **55**, 5936 (1990); [b] F. G. West and D. W. Willoughby, *J. Org. Chem.*, **58**, 3796 (1993); [c] F. G. West, P. V. Fisher, G. U. Gunawardena and S. Mitchell, *Tetrahedron Lett*, **34**, 4583 (1993).

[12a] P. Yates and W. J. Still, *J. Am. Chem. Soc.*, **85**, 1208 (1963); [b] P. Yates, M. J. Jorgenson and P. Singh, *J. Am. Chem. Soc.*, **91**, 4739 (1969); [c] N. Sugiyama, Y. Sato and C. Kashima, *Bull. Chem. Soc. Jpn.*, **43**, 3205 (1970); [d] S. C. Gupta and S. K. Mukerjee, *Tetrahedron Lett.*, 5073 (1973).

[13a] P. Yates and D. J. MacGregor, *Tetrahedron Lett.,* 453 (1969); [b] P. Yates and D. J. MacGregor, *Can. J. Chem.*, **51**, 1267 (1973).

[14] M. Shiozaki and T. Hiraoka, *Tetrahedron Lett.,* 4655 (1972).

[15] For a review see *e.g.*: F. B. Mallory and C. W. Mallory, Organic Reactions, Vol. **30**, John Willey and Sons, New York, 1984, p. 1.

[16] See *e.g.*: V. Baret, A. Gondini and E. Rousset, *J. Photochem. and Photobiol., A. Chemistry,* **103**, 169 (1997) and references cited therein.

[17] See *e.g.*: G. G. Aloisi, F. Elisei, L. Latterini, G. Marconi and V. Mazzucato, *J. Photochem. and Photobiol., A. Chemistry,***105**, 289 (1997).

[18a] See *e.g.*: [a] K. A. Muszkat, *Topics in Current Chemistry,* **88**, 89 (1980); [b] W. H. Laarhoven, *Recl. Trav. Chim., Pays-Bas,* **102**, 185 (1983); [c] R. Zertani and H. Meier, *Chem. Ber.*, **119**, 1704 (1986); [d] For a review see *e.g.*: Y. Tominaga and R. N. Castle, *J. Heterocyclic Chem.*, **33**, 523 (1996).

[19] See *e.g.*: [a] H. Schechter, W. J. Link and G. V. D. Tiers, *J. Am. Chem. Soc.*, **85**, 1601 (1963); [b] E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.,* **23**, 482 (1969); [c] W. H. Laarhoven Th. J. H. M. Cuppen and R. F. J. Nivard, *Tetrahedron*, **26**, 1069 (1970).

[20] M. H. Rossi, M. Yoshida, and J. G. S. Maia, *Phytochemistry*, **45**, 1263 (1997).

[21] D. I. Schuster, N. Kaprinidis, D. J. Wink and J. C. Dewan, *J. Org. Chem.* **56**, 563 (1991).

[22] It is obvious that distinction between structure **B** and **D** could be undoubtedly solved by X-ray structure determination but numerous fruitless attempts to obtain a useful crystal prevented the measurement by this technique.

[23] I. Škorić, Ž. Marinić and M. Šindler-Kulyk, *Heterocycles*, **53**, 55 (2000).

[24] Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-165912. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44/1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

[25] Nomenclature and abbreviations used are according to IUPAC rules: *Pure Appl. Chem*., **45**, 13 (1976).

[26] L. Spek: *HELENA,* Program for Data Reduction, University of Utrecht, Utrecht, The Netherlands, 1993.

[27] A. Altomare[1], G. Cascarano[1], C. Giacovazzo[1], A. Guagliardi[1], A. G. G. Moliterni[1], M. C. Burla[2], G. Polidori[2], M. Camalli[3], R. Spagna[3]: SIR 97, *A Package for Crystal Structure Solution by Direct Methods and Refinement*, [1]Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche, Bari, [2]Dipartimento di Scienze della Terra, Perugia, [3]Istituto di Strutturistica Chimica "G. Giacomello", Roma, Italy, 1997.

[28] G. M. Sheldrick: *SHELX97, Program for the Refinement of Crystal Structures*, Universität Göttingen, Germany, 1997.

[29] L. Spek, *PLATON98: A Multipurpose Crystallographic Tool*, 120398 Version, University of Utrecht, Utrecht, The Netherlands, 1998.

[30] C. K. Johnson: *ORTEPII*, Report ORNL-5138, Oak Ride National Laboratory, Tennessee, SAD, 1976.