Tetrahedron Vol. 48, No. 42, pp. 9323-9336, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00
Pergamon Press Ltd

Photochemical Behaviour of Furylidene Carbonyl Compounds

Maurizio D'Auria* (a), Andrea D'Annibale (b), Tommaso Ferri (b)

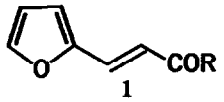
(a) CNR, Centro di Studio per la Chimica delle Sostanze Organiche Naturali, Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy.

(b) Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy.

(*Received in UK* 10 *August* 1992)

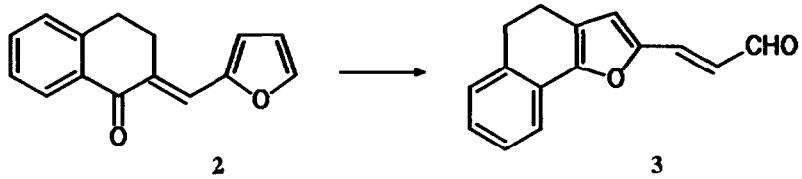
Abstract - Photophysical and electrochemical properties of furylidene carbonyl compounds were utilized in order to explain the observed photochemical behaviour.

Cinnamic acid gives photodimers when irradiated in the solid state: this reaction is stereospecific depending on the crystal form of the starting material.[1-4] However, the reaction of the same substrate in solution does not give any dimerization products but only *cis-trans* isomerization.[5,6] Recently we reported a new photochemical dimerization of 3-(2-furyl)acrylic derivatives **1** to give cyclobutanes.[7] This is the first example of photochemical dimerization of arylacrylic derivatives in solution in absence of Lewis acids:[8,9] in fact, in our experiments we used acetonitrile as solvent in the presence of benzophenone.



1

Furthermore, we have reported also that furylidenetetralones **2** do not give any dimerization product, but rather the isomerization product **3**.[10]

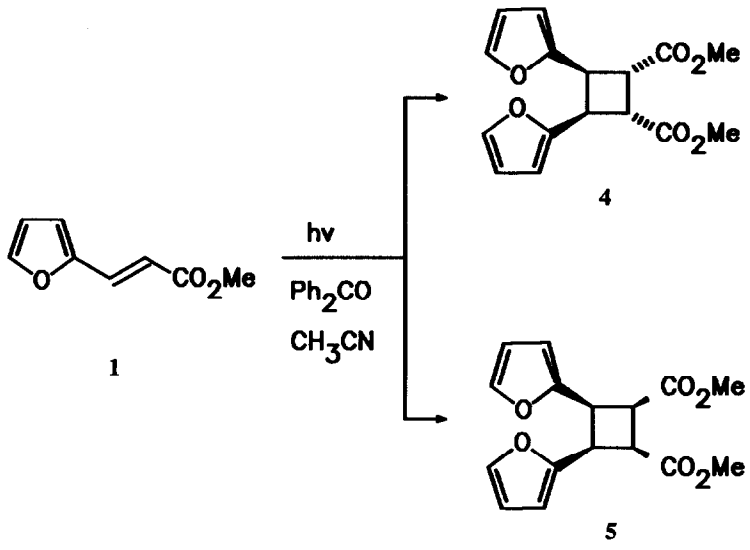


2 **3**

In this paper we report our results on the mechanism of these two reactions.

Results and Discussion

Irradiation of **1** in acetonitrile in the presence of benzophenone with a 500 W high pressure mercury arc in an immersion apparatus equipped with a Pyrex filter gave a mixture of **4** (61%) and **5** (27%).



Photochemical dimerization of coumarin (an arylacrylic acid derivative) in solution can be carried out using both direct and benzophenone sensitized conditions: under these different experimental conditions the reactions gave a mixture of *cis* head-to-head and *trans* head-to-head dimers.[11,12] The different results in these reactions can be explained in terms of the involvement of different excited states. *Cis* head-to-head dimer is formed from the singlet state, while *trans* head-to-head dimer from the triplet state. Furthermore, in the latter case singlet-singlet energy transfer from coumarin to benzophenone and subsequent triplet-triplet energy transfer from benzophenone to coumarin account for the role of benzophenone in this reaction.[13]

On the basis of these reported data we decided to study the photochemical dimerization of methyl 3-(2-furyl)acrylate in order to elucidate the role of benzophenone in our experiments and the solvent effect on product distribution.

Direct irradiation of **1** in an immersion apparatus equipped with a Pyrex filter allowed us to obtain a *cis-trans* photostationary equilibrium. In different solvents (acetonitrile, methanol, ethyl acetate, ethanol, and benzene) we observed the formation of 25 $\pm$ 1 % *cis*-isomer in the reaction mixture but no formation of any dimerization product. *Cis-trans* isomerization is a very fast reaction. As shown in Fig 1 the uv spectrum of **1** showed a strong absorption band at λ 299 nm (ε = 20000 $M^{-1}cm^{-1}$). When the substrate was irradiated with a mercury lamp without filter for a few seconds, shift of the peak at λ = 299 nm to λ = 302 nm was observed. This bathochromic shift is maintained even after prolonged irradiation. Laser flash photolysis experiments showed that direct irradiation of **1** in acetonitrile, ethanol, and benzene did not produce any transient state using both 308 and 347 nm excitations. The only photoproduct obtained by uv irradiation of **1** in benzene, ethanol, and acetonitrile was the *cis* isomer (characterized by GCMS); the photoisomerization quantum yield value (0.4 in benzene at λ_{exc} = 313 nm) evidences that the *trans* --> *perp* rotation is the main decay process of the excited states of **1**. Since there is no evidence of triplet state population under these experimental conditions, it strongly suggests that only the lowest singlet state is involved in the photoisomerization process.

We carried out dimerization reactions in the presence of benzophenone, the kinetic behaviour of which is shown in Fig. 2. The *cis* isomer rapidly reached 0.65 - 0.70 x 10^{-2} M concentration and maintained this concentration during all our experiments. Dimer formation followed a zero order kinetics in agreement with a sensitized reaction. We obtained k = 1.38 $\pm$ 0.02 x 10^{-3} M s^{-1}.

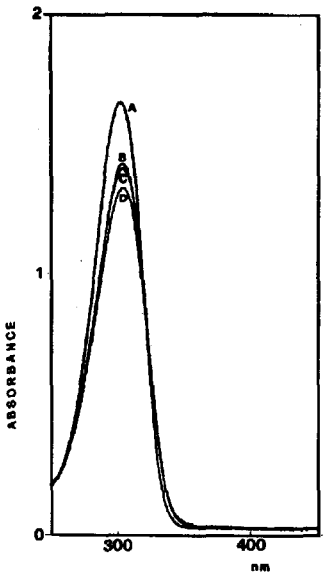


Fig. 1 - UV spectra of 1. **A**: spectrum in CH_3CN; **B**: spectrum after few seconds irradiation; **C**: spectrum after 3 min. irradiation; **D**: spectrum after 15 min. irradiation.

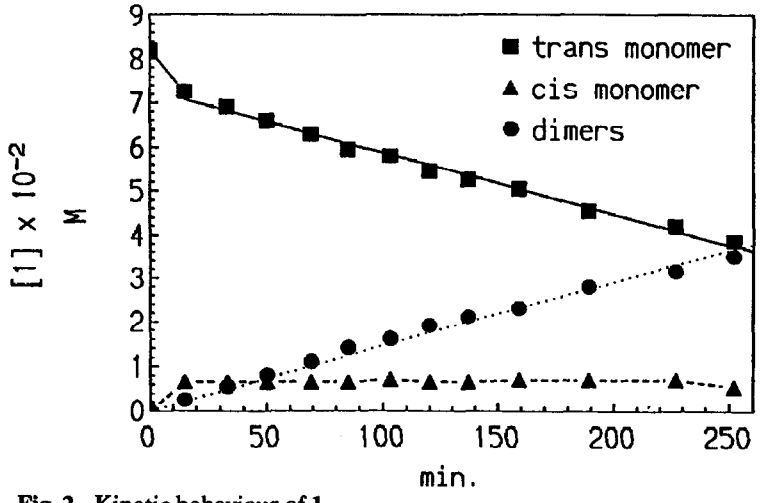


Fig. 2 - Kinetic behaviour of 1

These results were obtained by irradiating a 8.2 x 10^{-2} M solution of **1** in the presence of 3.43 x 10^{-3} M benzophenone in a Rayonet chamber reactor equipped with a Pyrex filter irradiating with lamps bearing a spectral output at 350 nm.

The zero order kinetics strictly depends on the benzophenone concentration. In fact, experiments in benzene at different benzophenone concentrations gave the results reported in Fig. 3. The quantum yields of dimer formation were 0.02 - 0.03.

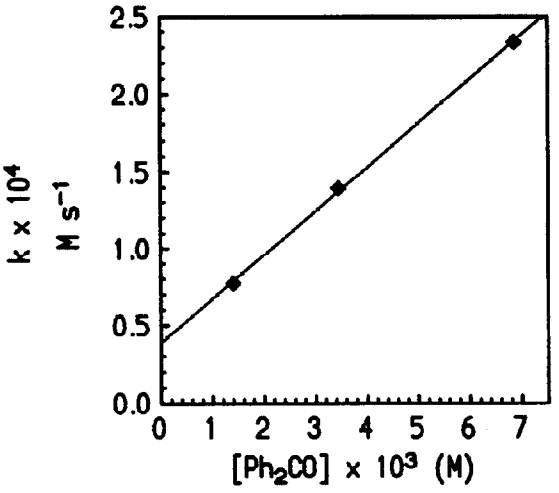


Fig. 3 - Correlation between dimerization kinetic constant and benzophenone concentration

As described above, we obtained only head-to-head and symmetric dimers **4** and **5**. In enone dimerization, excited charge-transfer complexes[14] or exciplexes,[15,16] favoured in polar solvents, explain the predominance of head-to-head dimers. Furthermore, change of the solvent is able to induce the predominance of head-to-tail dimers as a function of the dielectric constant of the solvent.[15,17]

The formation of charge-transfer complexes or exciplexes in the reaction was tested by performing some quenching experiments using 1,2,4-trimethoxybenzene: this compound shows a low $E_{1/2}^{Ox}$ value (0.82 V vs. $Ag/AgNO_3$ in CH_3CN)[18] and then can be a good quencher of electron transfer reactions: in fact, in the presence of 1,2,4-trimethoxybenzene we observed a sharp decrease of reaction quantum yield in the conversion **1** --> **4** + **5**.

In order to test an electron transfer mechanism when **1** has to be the donor, we determined the oxidation potential of **1**. It showed an anodic signal (Fig. 4) whose peak potential, vs. Ag/Ag^+ reference electrode, was 1.71 V.

We decided then to change the sensitizer using dicyanoanthracene (DCA)[19], a well-known electron-transfer sensitizer: in fact, on the basis of the Weller equation[20], considering $E_{1/2}^{Red}$(DCA) = - 0.89 V and ΔE_{exc}(DCA) = 2.88 eV[21], we obtained ΔG = - 0.49 eV. Therefore, we expected that DCA could be a good sensitizer for this reaction. However, we have found that DCA was unable to sensitize the conversion **1** --> **4** + **5**.

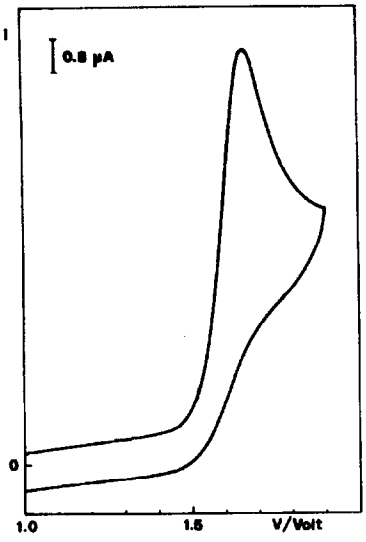


Fig. 4 - Cyclic voltammogram in acetonitrile solution of **1**.

In regards to the product distribution, we have carried out some experiments irradiating **1** in the presence of benzophenone in an immersion apparatus for 0.5 h. Change of the solvent did not modify the composition of the product mixture. The solvents tested were benzene (ε = 2.28), chloroform (ε = 4.81), ethyl acetate (ε = 6.02), *n*-butanol (ε = 17.8), ethanol (ε = 24.3), methanol (ε = 32.63), and acetonitrile (ε = 37.5).[22] In particular, we did not observe the formation of head-to-tail dimers.

Using laser flash photolysis apparatus in acetonitrile, the triplet of benzophenone (E_T = 69 kcal mol^{-1}) is efficiently quenched by **1**, which reduces its lifetime from ca. 4 μs to < 40 ns. In the meantime, a new transient species appears in the 380 nm region and decay with a lifetime of 140 ns (first-order kinetic). Since the same transient is sensitized by xanthone (E_T = 74 kcal mol^{-1}) (Fig. 5) and thioxanthone (E_T = 65 kcal mol^{-1}) it is assigned to the lowest triplet state of **1**. Its fast decay is in agreement with an efficient *trans* --> *perp* rotation.

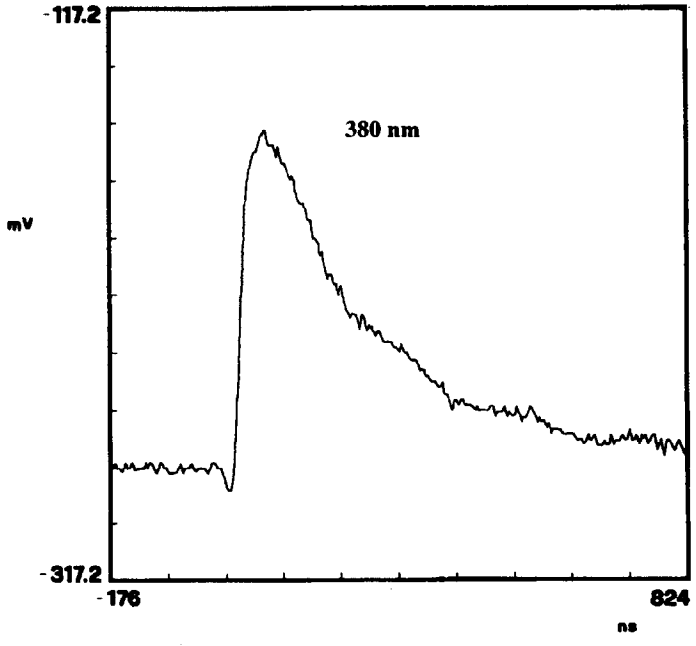
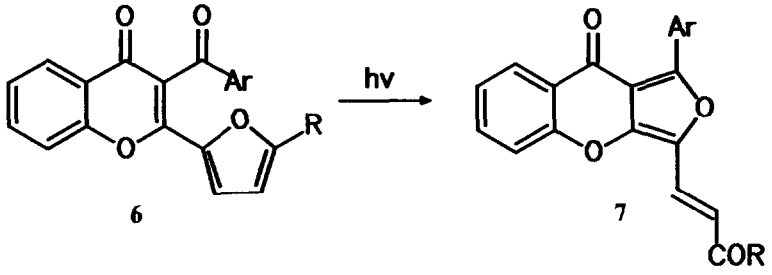


Fig 5 - Laser flash photolysis of **1**

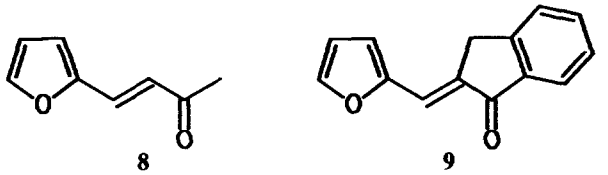
In ethanol, irradiation of benzophenone produces a triplet which has a much shorter lifetime (τ_T ca. 100 ns) and a ketyl radical ($\tau_{1/2}$ ca. 50 μs). Addition of **1** quenches benzophenone triplet to a τ_T < 30 ns with concomitant formation of a lowest excited triplet state of **1** at 380 nm. The decay of the ketyl radical is not influenced by the concentration of **1** even if its absorption is significantly reduced. In conclusion, it seems that furylacrylate dimerization reaction occurs in the triplet state of the molecule and that this triplet state is obtained via energy transfer from benzophenone. In this case we did not observe both any solvent effect in agreement with the above reported mechanism but in contrast with some reported dimerization reaction, and any datum in agreement with an electron-transfer mechanism. Finally, we did not find any evidence of a mechanism described in the case of coumarin dimerization.

In regards to the conversion **2** --> **3** the described behaviour induces some questions. First, it is not clear why in this case we did not observe any dimerization reaction. Then, the conversion **2** --> **3** occurs in good yields (56 - 60%), while the same procedure on 10^{-2} M solution of **6** in benzene resulted only in a 97% recovery of the starting material.[23]



6 **7**

Nevertheless, the above described reactions showed the same level of quantum yields: 0.040 $\pm$ 0.005 for the conversion **2** --> **3** and 0.044 for the conversion **6** --> **7**. Finally, it is not clear why **2** gives the described reaction while closely related structures such as furylidenacetone **8** and furylidenindanone **9** do not give any reaction.



8 **9**

Here we can not answer to all the questions but we want to report some data which can contribute to solve these questions.

We have reported[10] that the conversion **2** --> **3** occurred in the presence of benzophenone as sensitizer. We now report after many experiments performed under different conditions (see below) that no sensitization occurs.

Compound **2** showed an uv spectrum with absorptions at λ 372 (log ε 4.27) and 259 nm (log ε 4.13). Considering that direct irradiation experiments were performed using a Pyrex filter, only the absorption at 372 nm can be interested in photoisomerization reaction. The absorption at 372 nm was determined in EtOH. Changing the solvent we observed the behaviour described in Fig. 6 where we have reported $\Delta\nu_{max}$

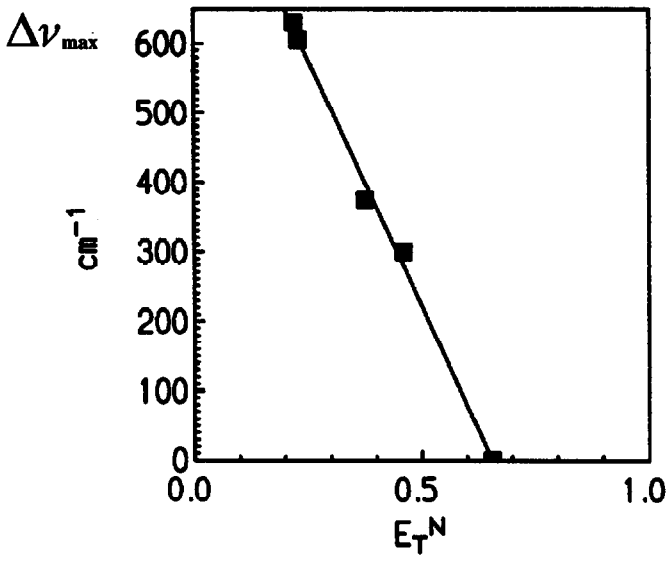


Fig. 6 - Correlation between $\Delta\nu_{max}$ in the UV spectrum of **1** in various solvents and E_T^N

in different solvents (ethanol, acetonitrile, acetone, 1,2-dimethoxyethane, and ethyl acetate) *vs* E_T^N.[24] We observed a shift to longer wavelengths related to solvent polarity in agreement with a π --> π^* transition.[25] Compound **2** showed a very low fluorescence emission at 465 nm (Φ_F 10^{-4}). This low fluorescence quantum yield can be due to the presence of *cis-trans* photoisomerization. The observed behaviour can be in agreement with the hypothesis that *cis-trans* isomerization occurred in the first excited singlet state.

We have tested *cis-trans* photoisomerization in different solvents in order to minimize this reaction. The results are reported in Table 1. These results were obtained by irradiating a 4.2 x 10^{-4} M solution of **2** for 1 h in a Rayonet chamber reactor equipped with a Pyrex filter and using lamps centred at 350 nm. The quantum yields of the conversion **2** --> **3** were determined on **2** as substrate in the same Rayonet chamber by using phenylglyoxylic acid as actinometer.[26]

We can see that in polar solvents the amount of *cis* isomer increases. Chloroform seems to be the best solvent for this reaction because no *cis-trans* isomerisation was observed. These data can be in agreement with a polar excited singlet state.

To investigate these feature we have studied electrochemical properties of this compound. Cyclic voltammetric experiments showed that on Pt **2** gives place to an irreversible (absence of cathodic peak) oxidation process. The oxidation peak potential is located at potential $\geq$ 1410 mV. In Fig. 7 two curves relative to this compound is reported.

As expected for an irreversible processes the peak potentials (Ep) shift towards more positive values increasing the scan rate (logarithmic dependence) as well as with the increasing of the concentration. The peak current intensities (Ip) show a linear dependence by the concentration for values > 10^{-4} mol l^{-1}.

The process is also complicated by adsorption of the reagent. In fact, as shown in Fig. 7, if after voltammogram (A) another one is recorded, waiting 30 s the obtained voltammograms is higher, while if after (B) a new voltammogram is recorded without waiting time a like (A) curve is obtained.

Table 1

Solvent	E_T^N [a]	*cis/trans*	$\Phi_{2-->3}$ [b]
Acetonitrile	0.460	0.76	0.040
DMF	0.404	0.66	0.043
Acetone	0.355	0.47	0.040
Chloroform	0.259	0	0.065
Ethanol	0.654	0.25	0.024
Ethyl acetate	0.228	0.47	0.047
Benzene	0.111	0.46	0.046

a) Ref. 24
b) $\pm$ 0.06

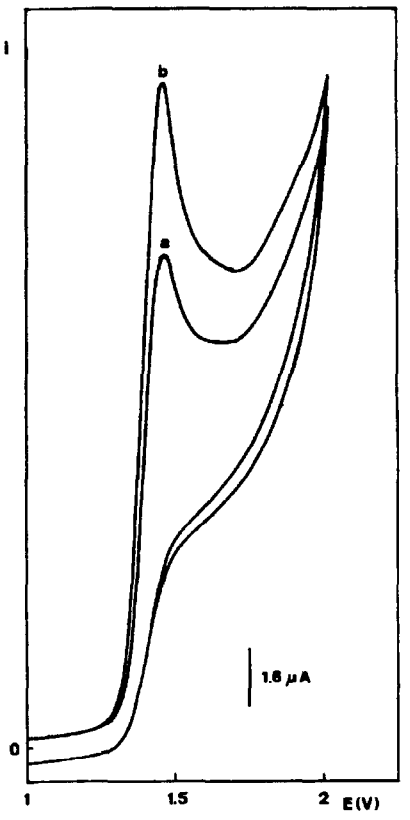


Fig. 7 - Cyclic voltammograms of 7.5×10^{-4} mol l^{-1} of **2** in CH_3CN containing 0.1 mol l^{-1} $NaClO_4$, A) recording the voltammogram immediately after the previous one, B) waiting 30' before to record the voltammogramms.

Polarographic experiments (cathodic scans on Dme) carried out in solutions at the same ionic strength (0.1 mol l^{-1}) in $CH_3CN:H_2O$ 1:1 showed that **2** has a behaviour as usual aryl alkyl carbonyl compounds[27,28] giving place to a wave corresponding to a monoelectronic charge transfer.

In Fig. 8 the curve at pH 9.2 (tris buffer) is shown. The wave is present in all pH range with exception of pH = 0 being the available potential range limited by hydrogen discharge; at higher pH values (> 9) the wave is actually splitted in more ones (usually two). This splitting is also well evidenced by DP polarograms (presence of more peaks); it shows in additions that double layer phenomena occur during first charge transfer: in fact, the first peak is higher that the other one/s) (Fig. 9).

In Fig. 10 the trend for Ep of several peaks of **2** is reported as function of pH. The Ep trend of the first peak is linear even if with different slope (ca. - 90 mV/pH at lower pHs and ca. - 45 mV/pH in neutral and alkaline range). The break point is the same of that of the second peak which is not pH dependent at pH higher than the break point.

The electrolysis of **2** was performed by controlling the potential at 1550 mV versus reference electrode. GCMS analysis of the electrolysis mixture showed that only isomeric compound was formed. This result is in agreement with the polar character of the intermediate involved in *cis-trans* isomerization of **2**.

Table 1 also furnishes some informations about the conversion **2** -- > **3**. The observed reactivity order is almost the inverse one of that determined for *cis-trans* isomerization. In conclusion *cis-trans* isomerization competes with the formation of the excited triplet state of **2** that is able to induce the photoisomerization **2** -- > **3**.

Then the question about difference between **2** and **6** can be answered. As reported above electrochemical properties of the substrate can play a role in the reactivity. At this purpose we have studied electrochemical properties of **9** a compound that does not give the same type of photoisomerization.

The oxidation peak potential is located at 1650 mV while reduction potential is only 30 mV more negative than that of **2** (Fig. 8). These differences are too low to justify the different behaviours. In a previous paper[10] we suggested that the different behaviour could be explained by considering that **2** showed steric hindrance to conjugation and that this steric hindrance could be alleviated in the product. We decided to verify this hypothesis on the basis of molecular mechanics calculations. By using Alchemy II (Tripos Associates) computer program we could calculate the strain energy of both compounds **2** and **3**. While **2** had a strain energy of 18.0 kcal mol^{-1}, **3** showed a value of 8.1 kcal mol^{-1} in agreement with our hypothesis. In Fig. 11 we can see **2** in order to estimate the above reported steric hindrance. This strain energy is not present in **9**.

In conclusion, in regards to the conversion **2** -- > **3** we have corrected our previous results and we have found that the reaction suffers from the medium. These results can be used to optimize the conversion. Furthermore, molecular mechanics results are in agreement with the hypothesis that the conversion is possible because there is a steric relief starting from substrate to the product.

Experimental

^1H and ^{13}C NMR were recorded with a Varian Gemini 200 MHz and a Varian XL300 spectrometers, using $CDCl_3$ as solvent. Mass spectra were obtained with a Hewlett-Packard 5971A mass selective detector connected with a Hewlett-Packard 5890 gas chromatographic instrument and with a Hewlett-Packard 9000 central processor. UV spectra were recorded with a Varian DMS-90 and with a Varian Cary 219 spectrophotometers. Fluorescence spectra were recorded using a Perkin-Elmer LS-5 spectrophotometer. IR spectra were obtained using a Perkin- Elmer 457 spectrophotometer. GLC analyses were performed with Hewlett-Packard 5880A and 5890 instruments (flame- ionization detector).

Starting Materials - 3-(2-Furyl)acrylic acid was converted into the methyl ester **1** by reaction of the corresponding acyl chloride[29] with MeOH in the presence of pyridine.[30] Bp 114 - 116 °C/18 mmHg (lit.,[31] 114 - 115 °C/16 mmHg); ^1H NMR ($CDCl_3$) δ: 7.50 (m, 1 H), 7.10 (d, 1 H, J = 16 Hz), 6.59 (d, 1 H, J = 4 Hz), 6.44 (dd, 1 H, J_1 = 2 Hz, J_2 = 4 Hz), 6.29 (d, 1 H, J = 16 Hz), 3.77 ppm (s, 3 H); IR (film, ν_{max}): 1720, 1645, 1560, 1485, 1435, 1390, 1310, 1275, 1260, 1210, 1200, 1168, 1075, 1040, 1020, 970, 930, 883, 860, 750, 730, 680 cm^{-1}; MS (*m/z*): 152 (M^+).

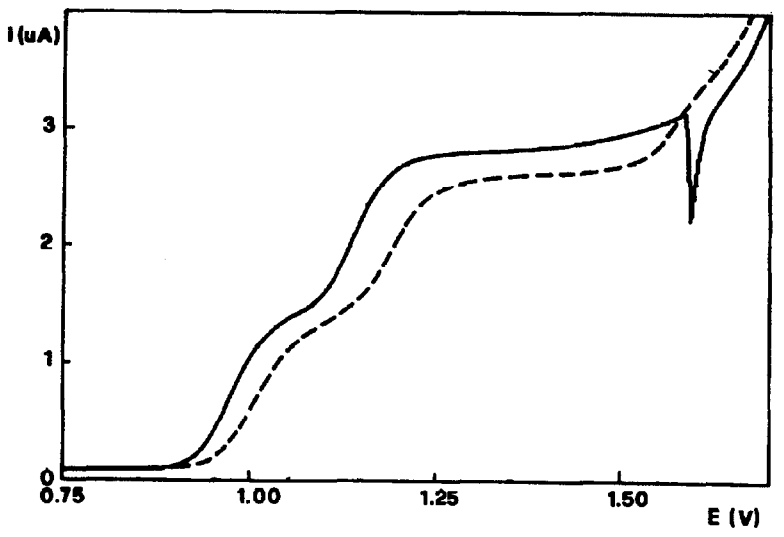


Fig 8 - Linear sweep polarograms on 1.2 x 10-4 mol l^{-1} of **2** (continuous line) and **9** (dotted line) in water:CH_3CN (1:1) at pH 9.2 (Tris buffer, ionic strength 0.1 mol l^{-1}).

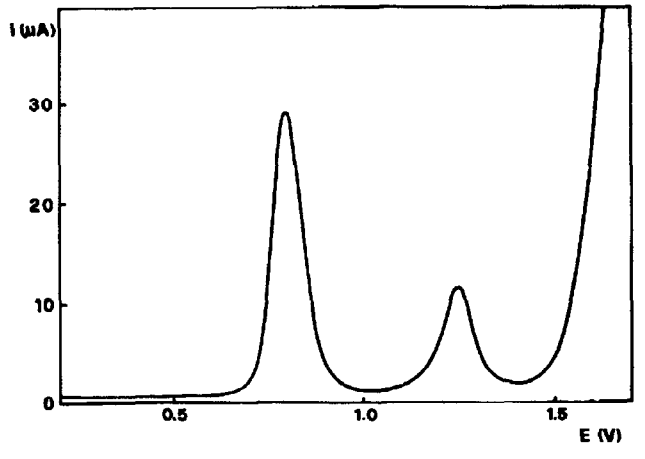


Fig. 9 - Differential pulse polarograms of 1.2 x 10-4 mol l^{-1} of **2** in water:CH_3CN (1:1) at pH 4.7 (acetic buffer ionic strength 0.1 mol l^{-1}).

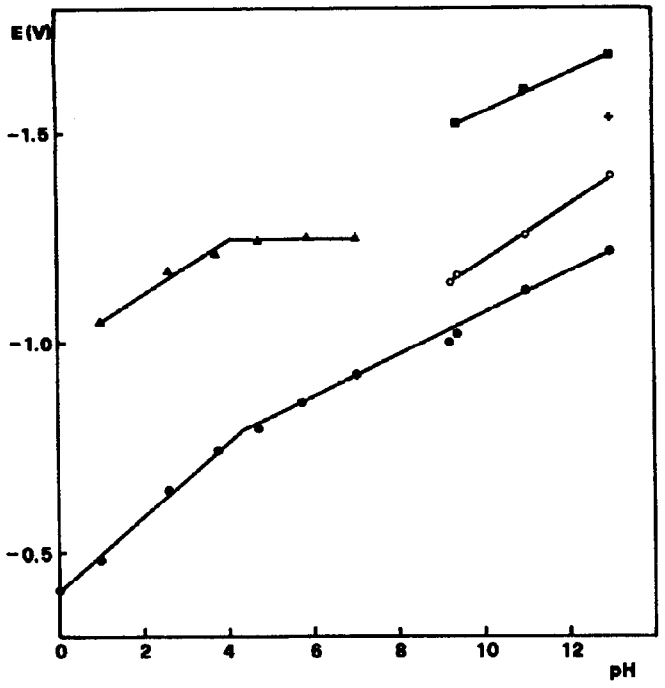


Fig. 10 - Trend of peak potential *vs* pH for **2** in mixed medium water:CH_3CN 1:1.

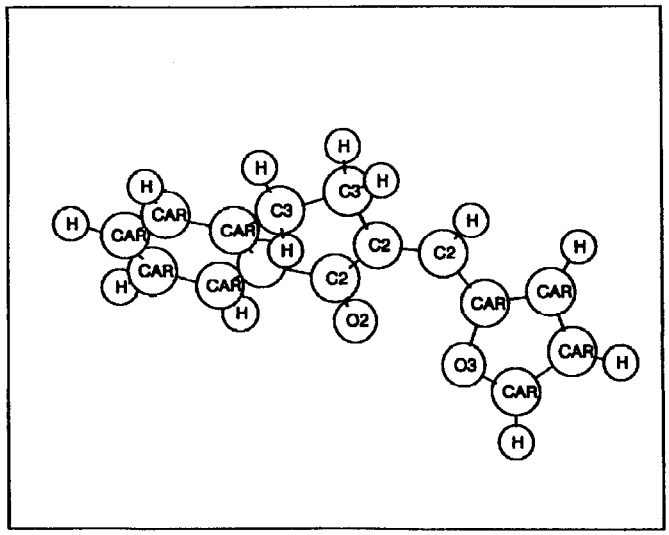


Fig. 11 - Compound **2**

Furylidentetralone **2** was obtained from 5-methyl-2-furancarbaldehyde by reaction with α-tetralone in aqueous alcoholic sodium hydroxide.[31] ^{1}H NMR ($CDCl_3$) δ: 8.08 (d, 1 H, J = 7.7 Hz), 7.52 (s, 1 H), 7.46 (dd, 1 H, $J_1 = J_2$ = 7.7 Hz), 7.32 (dd, 1 H, $J_1 = J_2$ = 7.7 Hz), 7.24 (d, 1 H, J = 7.7 Hz), 6.60 (d, 1 H, J = 3.2 Hz), 6.11 (d, 1 H, J = 3.2 Hz), 3.28 (t, 2 H, J = 7.0 Hz), 2.97 (t, 2 H, J = 7.0 Hz), 2.37 (s, 3 H); IR ($CHCl_3$, ν_{max}): 1670, 1610, 1570, 1460, 1440, 1375, 1360, 1335, 1320, 1300, 1160, 1135, 1020, 950, 930, 880 cm^{-1}; MS (*m/z*): 238 (M^+).

Synthesis of Cyclobutane derivatives 4 and 5 - **1** (1 g) was dissolved in acetonitrile (300 ml) in the presence of benzophenone (100 mg). The solution was outgassed with nitrogen for 1 h and then irradiated in an immersion apparatus with a 500 W high-pressure mercury arc (Helios- Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (6 h), the removal of the solvent under reduced pressure yielded a crude product that was chromatographed on silica gel. Elution with chloroform - *n*-hexane 3:2 gave pure **4** (61%) and **5** (27%). **4**: ^{1}H NMR ($CDCl_3$) δ: 7.32 (dd, 1 H, J_1 = 2 Hz, J_2 = 1 Hz), 6.25 (dd, 1 H, J_1 = 3 Hz, J_2 = 2 Hz), 6.12 (d, 1 H, J = 3 Hz), 3.74 (m, 1 H, J_{AX} = 10 Hz), 3.68 (s, 3 H), 3.51 ppm (m, 1 H, J_{AX} = 10 Hz); ^{13}C NMR ($CDCl_3$) δ: 172.06 (s), 153.02 (s), 142.13 (d), 110.27 (d), 106.58 (d), 52.08 (q), 42.92 (d), 39.56 ppm (d); IR (1% $CHCl_3$, ν_{max}): 1735, 1600, 1440, 1380, 1150, 1010, 950, 885 cm^{-1}; MS (*m/z*): 304 (4) (M^+), 160 (3), 152 (100%); **5**: ^{1}H NMR ($CDCl_3$) δ: 7.14 (m, 1 H), 6.11 (m, 1 H), 5.87 (m, 1 H), 4.17 (m, 1 H, J_{AX} = 7 Hz), 3.79 (m, 1 H, J_{AX} = 7 Hz), 3.65 ppm (s, 3 H); ^{13}C NMR ($CDCl_3$) δ: 172.38 (s), 152.66 (s), 141.80 (d), 110.21 (d), 106.97 (d), 52.06 (q), 42.92 (d), 38.31 ppm (d); IR (1% $CHCl_3$, ν_{max}): 1740, 1600, 1505, 1440, 1360, 1320, 1285, 1205, 1170, 1150, 1075, 1015, 910, 885 cm^{-1}; MS (*m/z*): 304 (4) (M^+), 160 (3), 152 (100%).

Synthesis of 3 - **2** (1 g) was dissolved in acetonitrile (300 ml) and the solution was outgassed with nitrogen for 1 h. The solution was irradiated in an immersion apparatus with a 500 W high-pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water jacket. At the end of the reaction (8 h) the removal of the solvent under reduced pressure yielded a crude product that was chromatographed on silica gel. Elution with benzene - Et_2O 9:1 gave pure **3** (57%). ^{1}H NMR ($CDCl_3$) δ: 7.54 (d, 1 H, J = 7.0 Hz), 7.34 (s, 2 H), 7.25 (d, 1 H, J = 15.7 Hz), 7.19 (m, 1 H), 6.67 (d, 1 H, J = 15.7 Hz), 6.60 (s, 1 H), 2.96 (t, 2 H, J = 7.8 Hz), 2.73 (t, 2 H, J = 7.8 Hz), 2.33 (s, 3 H); IR ($CHCl_3$, ν_{max}): 1665, 1625, 1605, 1585, 1565, 1485, 1450, 1425, 1360, 1305, 1255, 1170, 1125, 1090, 1000, 970, 910, 885 cm^{-1}; MS (*m/z*): 238 (M^+).

Quantum yields - The quantum yields were determined using phenylglyoxylic acid as actinometer. A 0.1 M solution of phenylglyoxylic acid in CH_3CN - H_2O (3:1) (50 ml) was irradiated for 600 s under nitrogen in a Pyrex tube which was surrounded by a Pyrex water-jacket connected to a Haake F3 thermostat to maintain the temperature at 25.0 ± 0.1 °C. A Rayonet apparatus with output centred at 350 nm was used for irradiation. The mixture was then extracted with CH_2Cl_2 and dried (Na_2SO_4). The removal of the solvent gave a crude product that was dissolved in $CDCl_3$ and analysed by ^{1}H NMR. The chemical conversion was calculated from the integrated *ortho* protons of the phenyl ring of phenylglyoxylic acid at δ = 8.1 and of benzaldehyde at δ = 7.9 with reference to the *meta* and *para* ring protons at δ = 7.6. Φ is assumed to be 0.7. Compound **1** or **2** and the sensitizer (if the reaction needs it) were dissolved in acetonitrile (or the other solvents used) (0.1 M solution in **1** or **2** and 0.01 M solution in the sensitizer) and 50 ml of this solution was irradiated in a Pyrex tube surrounded with a Pyrex water-jacket connected to a Haake F3 thermostat to maintain the temperature at 25.0 ± 0.1 °C in a Rayonet apparatus with output centred at 350 nm. After 600 s, the mixture was analysed by GLC (glass capillary column SPB-1, 30 m, oven temperature 100 - 250 °C, 30 °C min^{-1}).

Quenching experiments - Quenching experiments were performed using the same procedure above described for quantum yield determinations in the presence of 0.1, 1, and 10 equivalents of 1,2,4-trimethoxybenzene.

Electrochemical Properties - All voltammograms were performed by an Amel model 472 (Amel, Milan, Italy) polarograph equipped with a potentiostatic control, allowing potential scan rates up to 200

$mV\ s^{-1}$. As stationary working electrode a home made platinum electrode (spherically shaped with a surface of 0.795 mm^2) was used, while a mercury pool and an Ag, $AgCl/LiCl_{sat}$ (in CH_3CN) // $NaClO_4$ 0.1 M (in CH_3CN) were respectively used as counter[32] and reference electrode.[33] The voltammetric experiments were carried out in CH_3CN containing $NaClO_4$ (0.1 M) as supporting electrolyte. Controlled potential electrolysis experiments were performed by an Amel mod. 551 potentiostat coupled with an Amel mod. 731 electronic integrator. In this experiments the working electrode was a platinum foil of 7.5 x 17.5 x 0.1 mm. All the polarograms [linear sweep (LS) and differential pulse (DP)] were performed by an Amel mod. 433 polarograph controlled by a mod. 30 IBM PS/2 personal computer. In this experiments the potential of the dropping mercury working electrode was referred to an aqueous Ag, $AgCl/KCl_{sat}$ reference electrode and a platinum wire was the counter electrode. All polarographic experiments were performed using a dropping time of 1 s, a potential sweep rate of 5 $mV\ s^{-1}$ and a drop size of 20 a.u. (arbitrary units); furthermore - 50 mV of pulse height was used in DP experiments. The polarographic solutions were prepared by mixing (1:1) an aqueous solution (buffered at desidered pH and having in the mean time an ionic strength of 0.2 mol l^{-1}) with CH_3CN. As pH values of the polarographed solutions that of the aqueous buffered solutions were assumed. According the pH value to be obtained alternatively HCl, HCO_2H/HCO_2^-, $AcOH/AcO^-$, $H2PO4^-/HPO4^=$, TRIS, borax, and NaOH were alternatively used.

All the experiments were performed at room temperature (around 20 °C) on 25 ml of solution.

The solutions to be processed were at first bubbled with UPP nitrogen (just for few seconds in voltammetric experiments and for five minuts in polarographic ones). Then a nitrogen atmosphere was maintained above the solution (in order to prevent the contact with either oxygen or air humidity).

All reagents of anlytical grade from Carlo Erba or Merck were used without further purification. $NaClO4yH_2O$ was dried at 110 °C.

Laser Flash Photolysis - For laser flash photolysis study an Applied Photophysics apparatus was used. It utilizes an excimer laser (Lambda Physik EMG 50E) at 308 nm, an a Q- switched ruby laser (λ = 347.1 nm) as the exciting source. The analysing source was a pulsed high-pressure xenon lamp (250 W). Transient absorption signals were detected through a Baird Tatlock grating monochromator by a RCA 1P28 photomultiplier and observed on the screen of a Tektronix 468 oscilloscope. The decay curves were processed on a Cromenco 3102 computer. The pulse duration was about 20 ns and its energy was about 10 mJ. The detection system for the transient absorption spectra had a resolution of about 40 ns. The accuracy in lifetime measurements can be considered within 10%. In a running experiment, samples of **1** in the appropriate solvent were purged with nitrogen or argon before flashing. In order to obtain the transient spectra DA values were monitored immediately after the flash at intervals of 5 nm over the spectral range 380-700 nm and reproduced at least twice. All measurements were performed at room temperature (20 ± 2 °C).

Photostationary Equilibrium - *Cis-trans* photostationary equilibrium data in **1** were obtained by irradiating a 2.2 x 10^{-2} M solution of the compound in each solvent in an immersion apparatus with a 500 W high-pressure mercury arc (Helios- Italquartz) surrounded by a Pyrex water-jacket. After 6 -7 h the achievement of photostationary equilibrium was monitored by GLC (HP-1, 25 m capillary column, 100 - 250 °C, 30 °C min^{-1}).

Kinetic Behaviour of 1 - A 8.2 x 10^{-2} M solution of **1** in acetonitrile (50 ml) was irradiated in the presence of 3.43 x 10^{-3} benzophenone in a Rayonet chamber reactor equipped with a Pyrex filter. The lamps showed output centred at 350 nm. The formation of both *cis*-isomer and dimers was monitored by GLC (see above).

Acknowledgement

Dr. F. Elisei, Prof. U. Mazzuccato and all the staff of the Department of Chemistry of the University of Perugia (Italy) are gratefully ackowledged for laser flash photolysis experiments.

References

1. Stobbe, H.*Chem. Ber.*, **1919**, *52B*, 666.
2. Stobbe, H.; Bremer, A. *J. Prakt. Chem.*, **1929**, *123*, 1.
3. Schmidt, G. M. J. *Pure Appl. Chem.*, **1971**, *27*, 647.
4. Nakanishi, F.; Nakanishi, H.; Tsuchiya, M.; Hasegawa, M. *Bull. Chem. Soc. Jpn*, **1976**, *49*, 3096.
5. Curme, H. C.; Natale, C. C.; Kelley, D. J. *J. Phys. Chem.*, **1967**, *71*, 767.
6. Norval, M.; Simpson, T. J.; Bardashiri, E.; Howie, S. E. M. *Photochem. Photobiol.*, **1989**, *49*, 633.
7. D'Auria, M.; Piancatelli, G.; Vantaggi, A. *J. Chem. Soc. Perkin Trans. I*, **1990**, 2999.
8. Lewis, F. D.; Oxman, J. D. *J. Am. Chem. Soc.*, **1984**, *106*, 466.
9. Lewis, F. D.; Quillen, S. L.; Hale, D. D.; Oxman, J. D. *J. Am. Chem. Soc.*, **1988**, *110* , 1261.
10. D'Auria, M.; D'Onofrio, F.; Vantaggi, V. *Tetrahedron*, **1990**, *46*, 7831.
11. Anet, F. A. L.*Can. J. Chem.*, **1962**, *40*, 1249.
12. Schenck, G. O.; von Wilucki, I.; Krauch, C. H. *Chem. Ber.*, **1962**, *95*, 1409.
13. Hammond, G. S.; Stout, C. A.; Lamola, A. A. *J. Am. Chem. Soc.*, **1964**, *86*, 3103.
14. Wagner, P. J.; Bucheck, D. J. *J. Am. Chem. Soc.*, **1969**, *91*, 5090.
15. Loutfly, R. O.; de Mayo, P. *J. Am. Chem. Soc.*, **1977**, *99*, 3559.
16. Schuster, D. J.; Brown, P. B.; Capponi, L. J.; Rhodes, C. A.; Scaiano, J. C.; Tucker, P. C.; Weir, D. *J. Am. Chem. Soc.*, **1987**, *109*, 2533.
17. Challand, B. D.; de Mayo, P. *J. Chem. Soc. Chem. Commun.*, **1968**, 982.
18. Mattay, J. *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 825.
19. Beyer, H.; Fritsch, H. *Chem. Ber.*, **1941**, *74*, 494.
20. Mattay, J. *Synthesis*, **1989**, 233.
21. Gollnick, K.; Schnatterer, A. *Photochem. Photobiol.*, **1986**, *43*, 365.
22. 'CRC Handbook of Chemistry and Physics', R. C. Weast and M. J. Astle, Eds., 63rd Edition, CRC Press, Boca Raton, Florida, 1984.
23. Huffman, K. R.; Kuhn, C. E.; Zweig, A. *J. Am. Chem. Soc.*, **1970**, *92*, 599.
24. Reichardt, C. 'Solvents and Solvent Effects in Organic Chemistry', Verlag Chemie, Weinheim, 1988.
25. Botrel, A.; Corre, F.; Le Beuze, A. *Chem. Phys.*, **1983**, *74*, 383.
26. Defoin, A.; Defoin-Straatman, R.; Hildebrand, K.; Bittersmann, E.; Kreft, D.; Kuhn, H. J. *J. Photochem.*, **1986**, *33*, 237.
27. Milner, G. W. C. 'The Principle and Application of Polarography', Longmans, London, 1959, p. 501.
28. Zuman, P. 'Topics in Organic Polarography', Plenum Press, London, 1970, p. 37.
29. Sasaki, T. *Biochem. Zh.*, **1910**, *25*, 272.
30. Bartlett, P. D.; Ross, S. D. *J. Am. Chem. Soc.*, **1947**, *69*, 460.
31. Dunlop, A. P.; Peters, F. N. 'The Furans', Reinhold Publishing Co., New York, 1953.
32. Mann, K. C. *Non Aqueous Solvents for Electrochemical Use*, in 'Electrochemical Analysis', A. J. Bard Ed., Marcel Dekker, New York, 1969, vol. 3, p. 60.
33. Vedel, J.; Tremillon, B. *J. Electroanal. Chem.*, **1959/60**, *1*, 241.