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PHOTOCHEMISTRY OF FURANS. PHOTOCHEMICAL TRANSFORMATIONS OF SOME SUBSTITUTED 2-PHENYL-3-FURYLACRYLIC ACIDS†

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Abstract—A number of new substituted 2-phenyl-3-furylacrylic acids (**1–14**) were synthesized by modified Perkin reaction and separated into their *E*-and *Z*-isomers and identified by spectroscopic methods. *E*-isomers were UV-irradiated under aerobic conditions to give several types of photoproducts, ie substituted naphtho[2,1-*b*]furancarboxylic acids (*B*), 2,3-epoxy-2,3-dihydrofuro[3,2-*b*]pyran-5-ones (*C*), 7a - hydroxy - 3a,7a - dihydrofuro[3,2 - *b*]pyran - 5 - ones (*D*) and 7a - hydroperoxy - 3a,7a - dihydrofuro[3,2 - *b*]pyran - 5 - one (*E*) were recognized. The type of product and yield are strongly substituent-dependent.

Diarylethylenes and similar compounds have been a subject of photochemical investigation for many years. Their usual reactions initiated by light can be systematized as dimerizations, isomerizations and cyclizations. As a result of a broad interest many aspects of their photochemistry are now understood.[2] Special interest has been paid to the photochemistry of cinnamic acid and its derivatives. Besides mentioned types of reaction,[3–5] lactonizations[6] were also observed. In the context of the present paper dehydrocyclizations of 2-styrylfurane[7] and 1,2-di-(2-furyl)-ethylene[8] as well as their substituted analogues[9,10] have to be pointed out.

In addition to reactions mentioned above, excited heteroaryl-substituted ethylenes are supposed to interact with oxygen. The interaction of oxygen with electronically excited states of organic molecules can result in many interesting transformations. In many processes explanation may involve some kind of reaction with singlet oxygen[11] but oxidations through the intervention of superoxide radical anion were also suggested.[12,13]

Continuing our studies of the chemistry of furans[14] our interest has been directed to the photochemistry of furan

Table 1. UV Irradiation of 2-Aryl-3-furylacrylic acids

Starting acid (A)[a]			Irrad.	Product	Yield	Regener.
No	R_1	R_2	(hrs)		%	acid (A)
1	H	4-CH_3	48	B + C	30+30	-
2	H	3-CH_3	67	-	-	67
3	H	4-OCH_3	72	-	-	15
4	H	3-OCH_3	100	B	50	-
5	H	4-Cl	48	C	15	30
6	H	3-Cl	125	-	-	-
7	H	4-NO_2	98	-	-	80
8	5-CH_3	4-CH_3	48	-	-	-
9	5-CH_3	3-CH_3	48	D	40	-
10	5-CH_3	4-OCH_3	48	E[b]	48	-
11	5-CH_3	3-OCH_3	96	-	-	-
12	5-CH_3	4-Cl	48	D	60	10
13	5-CH_3	3-Cl	72	-	-	-
14	5-CH_3	4-NO_2	30	-	-	-

[a] E-isomers of acids were used.

[b] The same product was obtained in sensitized reaction but yield after 24 hrs of irradiation was 70%.

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analogues of cinnamic acid, i.e. furylacrylic acid and derivatives.[15,16] In case of 2-aryl-substituted derivatives we observed usual photoreactions of diarylethylene, but due to the π-system in which furane nucleus is conjugated with ethylenic double bond a photooxygenation could be supposed as well if oxygen was present.

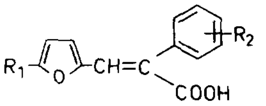
RESULTS AND DISCUSSION

2-Aryl-3-furylacrylic acids **1–14** (Table 2) were prepared by standard procedures. Both, *E* and *Z* isomers were separated, purified and identified by microanalyses and/or spectroscopic methods.

Our previous experiments with several compounds of this type in absence of oxygen showed almost exclusively *cis–trans* photoisomerization.[15] In aerobic conditions the most prominent photochemically induced reaction was dehydrocyclization,[16] potentially useful as a method for the preparation of substituted naphtho[2,1-*b*]furan-8-carboxylic acid and derivatives. However, in several instances we realized that the reaction is strongly substituent dependent and competes with possible lactonization (Fig. 1) effected by expected attack of carboxylic group on the furan nucleus. Spectroscopic data obtained for products of lactonization in our experiments indicated δ-lactone structure, i.e. compounds with anelated furane and 2-pyrone nucleus. Such structures, by the way, were found in some natural products.[19]

Regarding photolactonization it should be noted that in the case of substituted 2-phenylcinnamic acid the formation of β-lactone was reported.[6] The only previous

Table 2. 2-Aryl-3-furylacrylic acids



No	R_1	R_2	Isomer	M.p. °C	Yield %	Formula	Anal. calc'd found %C	%H
1	H	4-CH_3	E^{17}	205-6				
			Z^{17}	131-2				
2	H	3-CH_3	E	142-3	55	$C_{14}H_{12}O_3$	73.67	5.30
							73.83	5.12
			Z	96-7	3		73.82	5.08
3	H	4-OCH_3	E	175	88	$C_{14}H_{12}O_4$	69.75	5.46
							69.50	5.32
			Z	130	5		69.49	5.49
4	H	3-OCH_3	E	170-1	34	$C_{14}H_{12}O_4$	69.75	5.46
							69.47	5.07
			Z	98-100	5		70.03	5.66
5	H	4-Cl	E^{17}	206-7				
			Z^{17}	104-5				
6	H	3-Cl	E	159-60	55	$C_{13}H_9ClO_3$	62.79	3.65
							62.49	3.38
			Z	105-6	18		63.07	3.92
7	H	4-NO_2	E^{17}	235-6				
			Z^{17}	157-8				
8	CH_3	4-CH_3	E	165-7	86	$C_{15}H_{14}O_3$	74.36	5.82
							74.29	5.58
			Z	138	5		74.10	5.98
9	CH_3	3-CH_3	E	155-7	71	$C_{15}H_{14}O_3$	74.36	5.82
							74.30	5.52
			Z	110-2	5		74.44	5.57
10	CH_3	4-OCH_3	E	158-60	67	$C_{15}H_{14}O_4$	69.75	5.46
							69.50	5.32
			Z	104	4		69.49	5.59
11	CH_3	3-OCH_3	E	149-50	36	$C_{15}H_{14}O_4$	69.75	5.46
							69.92	5.57
			Z	88-89	1		69.67	5.32
12	CH_3	4-Cl	E	172-4	58	$C_{14}H_{11}ClO_3$	64.25	3.85
							64.10	3.78
			Z	122-4	3		64.40	3.99
13	CH_3	3-Cl	E	165	43	$C_{14}H_{11}ClO_3$	64.25	3.85
							64.38	3.67
			Z	120-1	1		64.03	3.97
14	CH_3	4-NO_2	E^{18}	210-4	52			
			Z^{18}	196-8	3			

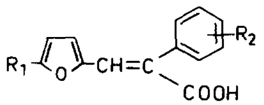
example of photochemical δ-lactone formation was reported in case of transformation dihydroxy-substituted 2-phenylcinnamic acid to six membered lactone Esculetin.[20]

Soon after starting the present work we realized that in examples studied the structure of formed δ-lactones must be more complex than supposed, and that some kind of oxygenation took place.

Due to characteristic absorbances of 1–14 (Table 3) it was found convenient to conduct irradiations with a pyrex filtered light or "Rayonet" reactor equipped with 300 nm lamps. Compounds in benzene and in methanolic solution (10 and 12) were irradiated while air was bubbled through the solution. After irradiation the reaction mixture was worked up and separated products submitted to structure determinations by means of MS, UV IR and ^{1}H NMR spectra.

We propose the formation three of possible "oxygenated" δ-lactones (*C*, *D* and *E*) and/or product of dehydrocyclization (*B*) (Fig. 2). The type of the product,

Table 3. UV and IR spectroscopic data for 2-Aryl-3-furylacrylic acids



No	R_1	R_2	(E)-ISOMER $\lambda_{max}(\log\varepsilon)$ (nm)	(E)-ISOMER $\nu_{C=C}$ (cm^{-1})	(E)-ISOMER $\nu_{C=O}$ (cm^{-1})	(Z)-ISOMER $\lambda_{max}(\log\varepsilon)$ (nm)	(Z)-ISOMER $\nu_{C=C}$ (cm^{-1})	(Z)-ISOMER $\nu_{C=O}$ (cm^{-1})
1[17]	H	4-CH_3	230(3.91) 305(4.26)	1520	1665	235(3.93) 242(3.84)	1600	1695
2	H	3-CH_3	205(4.07) 233(3.95) 305(4.24)	1580	1640	208(4.18) 237(3.92) 318(4.32)	1665	1695
3	H	4-OCH_3	200(4.24) 225(3.97) 309(4.27)	1587	1650	207(4.28) 222(4.19) 234(4.22) 242(4.09) 313(4.25)	1650	1690
4	H	3-OCH_3	201(3.97) 218(4.02) 310(4.23)	1590	1670	212(4.05) 240(3.92) 318(4.27)	1580	1720
5[17]	H	4-Cl	235(3.97) 307(4.27)	1600	1660	235(3.93) 242(3.90) 320(4.59)	1610	1690
6	H	3-Cl	222(4.03) 248(3.92) 311(4.18)	1600	1670	208(4.03) 240(3.97) 320(4.20)	1590	1670
7[17]	H	4-NO_2	258(4.39)	1600	1665	275(4.09) 372(4.32)	1580	1695
8	CH_3	4-CH_3	203(4.26) 232(3.91) 238(3.91) 326(4.45)	1600	1650	204(4.22) 235(3.90) 244(3.84) 328(4.47)	1550	1650
9	CH_3	3-CH_3	203(4.03) 225(3.90) 325(4.38)	1560	1634	208(4.30) 230(4.02) 325(4.42)	1616	1674
10	CH_3	4-OCH_3	200(3.96) 224(4.05) 326(4.36)	1600	1660	202(4.29) 237(4.01) 330(4.53)	1660	1709
11	CH_3	3-OCH_3	203(4.02) 216(3.99) 240(3.87) 326(4.28)	1600	1670	220(3.92) 255(3.82) 326(4.56)	1620	1700
12	CH_3	4-Cl	202(4.24) 238(3.85) 328(4.34)	1600	1670	203(4.11) 212(3.97) 235(3.84) 331(4.49)	1610	1680
13	CH_3	3-Cl	212(4.08) 243(3.93) 328(4.12)	1616	1670	212(4.07) 242(3.93) 322(4.33)	1630	1700
14	CH_3	4-NO_2	200(4.38) 310(4.27)	1600	1664	200(4.34) 385(4.38)	1588	1670

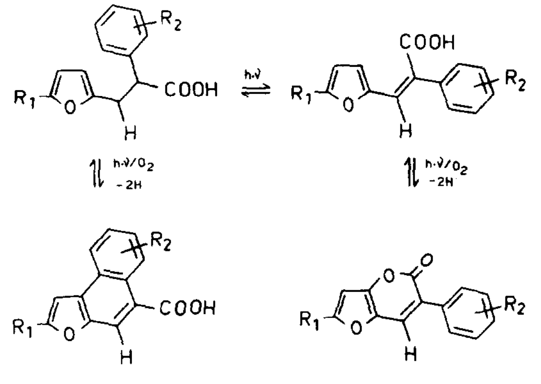


Fig. 1.

yield and composition of the possible mixture was strongly substituent dependent (Table 1). Though profound resinifiaction or decomposition took place preventing firm conclusion in some of irradiation experiments, it seems that δ-lactonization in studied examples is always accompanied with oxygenation before or after lactonization (Fig. 2). It should be mentioned that in some instances such reactions were accompanied or overwhelmed by dehydrocyclization to corresponding naphtho[2,1-*b*]furancarboxylic acids *B* (**15**, **16**, **18**, **20**).

The transformation A → C with initial cyclization (lactonization) effected by 1,5-hydrogen shift and subsequent 1,2-epoxidation took place if the furan nucleus bore no substituent in position 5. Such a reaction was confirmed with **1** and **5** (p-methyl and p-chloro substituted aryl group). Other furan-unsubstituted compounds reacted only sluggishly leaving mostly unchanged starting product or profound decomposition took place (Table 1).

The structure of epoxydihydrofuropyrones **17** and **19** (Fig. 2, structure C) were deduced from spectral data. The mass spectrum of **17** and **19** showed an $M^{+\cdot}$ peak at *m/e* 242 (100%) as well as 264 (8%) and 262 (20%) respectively. The ^{1}H NMR spectra of **17** showed two 1H doublets at δ 6.34, and δ 7.42 ($J = 5$ Hz) assigned to epoxyde-ring protons. Signals of two epoxyde-ring protons for **19** were recognized as doublets at δ 6.62 and 7.75 ($J = 6$ Hz).

The result of oxidative photochemical reaction was quite different if substituted furan compound, i.e. 3-(5-methyl-2-furyl)-2-arylacrylic acids were used (**8–14**). Instead of corresponding epoxydihydrofuro[3,2-*b*]pyrones the only isolable oxidized products were hydroxydihydrofuro[3,2-*b*]pyrones **21** and **22**. (Fig. 2, structure D) or their hydroperoxy-analogue **23** (Fig. 2, structure E). Hydroxy-dihydrofuropyrones (**21** and **22**) were obtained if 3-tolyl or 4-chlorophenyl group was present in starting acid (**9** and **12**, respectively).

The mass spectra showed a very weak $M^{+\cdot}$ at *m/e* 258 for **21**, and *m/e* 280 and 278 for **22**. From ^{1}H NMR spectra most significant were singlets at δ 10.99 and δ 11.03 disappearing on addition of D_2O (hydroxyl proton) as well as an AB pattern (protons H-3 and H-3a at δ_A 6.17, δ_B 6.35 (2H, $J_{AB} = 5.4$ Hz) and δ_A 6.21, δ_B 6.39 (2H, $J_{AB} = 5.4$ Hz), respectively. Similarly, as with epoxydihydrofuropyrones, the proposed δ-lactone structures were supported by IR spectra ($\nu_{C=O}$ in the range of 1745–1780 cm^{-1}).

An unexpected result was observed with 2 - (4 - methoxyphenyl) - 3 - (5 - methyl - 2 - furyl)acrylic acid **10** which yielded 7a-hydroperoxy-dihydrofuropyrone **23** as sole isolable product.

Similarly, as with **21** and **22**, the ^{1}H NMR spectrum of **23** showed an AB proton pattern δ_A 6.15 and δ_B 6.28 (2H, $J_{AB} = 6.0$ Hz) as well as 1H singlet at 10.92 (disappeared on addition of D_2O) accounting for hydroperoxy proton, but most indicative was the mass spectrum which exhibited $M^{+\cdot}$ at *m/e* 290. Other 5-methylfuryl derivatives (**8**, **11**, **13** and **14**) decomposed under the experimental conditions.

It is well known that many reactions of oxygen with conjugated π-systems may be explained by initial 1,4-addition of photochemically generated $^1O_2$, and as a matter of fact 1,4-addition of singlet oxygen to the furan nucleus with formation of an "ozonide" type peroxide is well documented.[21] In our case such a reaction has to be rejected since the formation of hydroperoxy-γ-lactone with spiro-structure (F) which ought to be formed after internal attack of carboxyl group was not detected.

Experiments carried out in the presence of sensitizer (Bengal Rose) in methanolic solution, known to stimulate $^1O_2$ formation, showed a fast and complete decomposition of all acrylic acids except **10**. The product of sensitized reaction with **10** was the same as in the absence of sensitizer, but notable speeding of the reac-

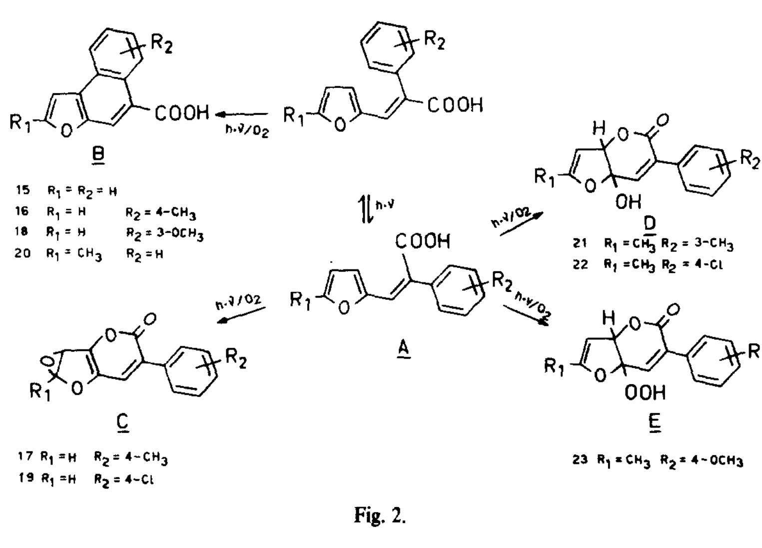
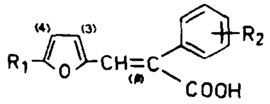


Fig. 2.

Table 4. ^{1}H NMR data for 2-aryl-3-furylacrylic acids



No	R_1	R_2	Isomer	$H^{a)}$ calc'd$^{b)}$ found	$H_{CH_3}^{a)}$	$H_{OCH_3}^{a)}$	$H_3^{a)}$	$H_4^{a)}$	$H_{arom.}^{a)}$ + $H_5^{a)c)}$
2	H	3-CH_3	E	7.68 7.80	2.37(3H,s)	-	5.80(1H,d) $J_{3,4}$=3.6	6.24(1H,q) $J_{3,4}$=3.6 $J_{4,5}$=1.8	6.8-7.5(5H,m)
			Z	7.31 6.84	2.38(3H,s)	-	6.70(1H,d) $J_{3,4}$=3.4	6.36(1H,q) $J_{3,4}$=3.4 $J_{4,5}$=1.6	6.7-7.4(5H,m)
3	H	4-OCH_3	E	7.68 7.77	-	3.84(3H,s)	5.94(1H,d) $J_{3,4}$=3.9	6.28(1H,q) $J_{3,4}$=3.9 $J_{4,5}$=1.8	6.8-7.4(5H,m)
			Z	7.31 6.75	-	3.82(3H,s)	6.68(1H,d) $J_{3,4}$=3.6	6.42(1H,q) $J_{3,4}$=3.6 $J_{4,5}$=1.6	6.93(2H),7.20(2H) $J_{A_2B_2}$=9.0 7.37(1H,d) $J_{3,4}$=1.6
4	H	3-OCH_3	E	7.68 7.80	-	3.80(3H,s)	5.90(1H,d) $J_{3,4}$=3.5	6.28(1H,q) $J_{3,4}$=3.5 $J_{4,5}$=1.7	6.8-7.5(5H,m)
			Z	7.31 6.80	-	3.75(3H,s)	6.70(1H,d) $J_{3,4}$=3.4	6.38(1H,q) $J_{3,4}$=3.4 $J_{4,5}$=1.7	6.9-7.4(5H,m)
6	H	3-Cl	E	7.68 7.83	-	-	6.00(1H,d) $J_{3,4}$=3.8	6.32(1H,q) $J_{3,4}$=3.8 $J_{4,5}$=1.8	7.0-7.5(5H,m)
			Z	7.31 7.30	-	-	6.80(1H,d) $J_{3,4}$=3.0	6.38(1H,q) $J_{3,4}$=3.0 $J_{4,5}$=1.6	7.1-7.5(5H,m)
8	CH_3	4-CH_3	E	7.68 7.64	2.40(3H,s) 2.22(3H,s)	-	5.80(1H,d) $J_{3,4}$=4.0	5.70(1H,d) $J_{3,4}$=4.0	7.02(2H),7.14(2H) $J_{A_2B_2}$=7.0
			Z	7.31 6.71	2.36(3H,s) 2.29(3H,s)	-	6.60(1H,d) $J_{3,4}$=4.0	5.99(1H,d) $J_{3,4}$=4.0	7.00(2H),7.40(2H) $J_{A_2B_2}$=8.5
9	CH_3	3-CH_3	E	7.68 7.77	2.21(3H,s) 2.36(3H,s)	-	5.76(1H,d) $J_{3,4}$=3.8	5.90(1H,d) $J_{3,4}$=3.8	6.9-7.4(4H,m)
			Z	7.31 6.84	2.30(3H,s) 2.40(3H,s)	-	6.76(1H,d) $J_{3,4}$=3.8	6.10(1H,d) $J_{3,4}$=3.8	7.3-7.4(4H,bs)
10	CH_3	4-OCH_3	E	7.68 7.73	2.20(3H,s)	3.82(3H,s)	5.86,(2H,s)		6.93(2H),7.17(2H) $J_{A_2B_2}$=9.0
			Z	7.31 6.72	2.28(3H,s)	3.80(3H,s)	6.65(1H,d) $J_{3,4}$=3.0	6.03(1H,d) $J_{3,4}$=3.0	6.88(2H),7.42(2H) $J_{A_2B_2}$=9.0
11	CH_3	3-OCH_3	E	7.69 7.73	2.20(3H,s)	3.76(3H,s)	5.90(1H,d) $J_{3,4}$=3.8	5.87(1H,d) $J_{3,4}$=3.8	6.7-7.5(4H,m)
			Z	7.31 6.78	2.27(3H,s)	3.80(3H,s)	6.68(1H,d) $J_{3,4}$=3.8	6.05(1H,d) $J_{3,4}$=3.8	6.8-7.4(4H,m)
12	CH_3	4-Cl	E	7.68 7.75	2.22(3H,s)	-	5.98(2H,s)		7.20(2H),7.39(2H) $J_{A_2B_2}$=8.0
			Z	7.31 6.75	2.30(3H,s)	-	6.72(1H,d) $J_{3,4}$=3.6	6.03(1H,d) $J_{3,4}$=3.6	7.27(2H),7.43(2H) $J_{A_2B_2}$=6.0

Table 4 (*contd.*)

No	R_1	R_2	Isomer	$H^{a)}$ calc'd$^{b)}$ found	$H_{CH_3}^{a)}$	$H_{OCH_3}^{a)}$	$H_3^{a)}$	$H_4^{a)}$	$H_{arom.}^{a)}$ + $H_5^{a)c)}$
13	CH_3	3-Cl	E	7.68 7.72	2.18(3H,s)	-	5.87(1H,d) $J_{3,4}$=3.5	5.98(1H,d) $J_{3,4}$=3.5	7.0-7.4(4H,m)
			Z	7.31 6.80	2.32(3H,s)	-	6.80(1H,d) $J_{3,4}$=3.0	6.10(1H,d) $J_{3,4}$=3.0	7.2-7.5(4H,m)
14[18]	CH_3	4-NO_2	E	7.68 7.71	2.12(3H,s)	-	6.08(1H,d) $J_{3,4}$=3.5	6.20(1H,d) $J_{3,4}$=3.5	7.60(2H),8.30(2H) $J_{A_2B_2}$=9.0
			Z	7.31 7.10	2.32(3H,s)	-	6.77(1H,d) $J_{3,4}$=3.0	6.22(1H,d) $J_{3,4}$=3.0	7.80(2H),8.26(2H) $J_{A_2B_2}$=9.0

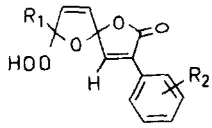
s = singlet, d = doublet, q = quartet, bs = broadened singlet

a) Chemical shift given in ppm (δ); Coupling constants given in Hz.

b) Calculated according to U.E. MATTER at all.[26]

c) For comp. 2, 3, 4 and 6.

tion reduced decomposition and better yield of **23** was noticed. Though more has to be done to explain the mechanism of these reactions with certainty, we would suggest that in transformation **A**→**D** and **A**→**E** (5-methyl-substituted furan ring) 1,2-addition of oxygen with epoxidation or peroxidation at position 2,3 of the



F

furan nucleus, preceded cyclization. Such an explanation could be supported by some related observations.[22–25] Subsequent internal attack of carboxyl group would open epoxide or peroxide ring yielding isolated hydroxy (**21** and **22**) or hydroperoxy (**23**) δ-lactones. On the contrary if there was no methyl group substituted at position 5 of the furan nucleus (transformation **A**→**C**) we believe δ-lactonization must be an initial step leaving bond 2,3 free for oxygenation to corresponding epoxides **17** and **19**.

EXPERIMENTAL

M.ps are uncorrected. The IR spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrophotometer in KBr discs. The UV spectra were taken on a Perkin-Elmer 124 spectrophotometer using ethanolic solution. The ^1H NMR spectra were recorded on a Varian T-60 or Joel J.M.M.-FX 100 FT spectrometer with tetramethylsilane as the internal reference. Mass spectra were obtained with Varian MAT-CH7 spectrometer operating at 70 eV by direct insertion probe. Irradiations were performed with a water cooled immersion well equipped with "Original Hanau" 125 W high pressure mercury arc lamp using pyrex filter, or inside a "Rayonet" photochemical reactor provided with 300 or 254 nm lamps as specified.

General procedure for preparing 2-aryl-3-furyl-acrylic acids (**4–14**)

Substituted phenylacetic acids (0.1 mole) and corresponding furaldehydes (0.12 mole) in a mixture of triethylamine (20 ml) and acetic anhydride (20 ml) was heated for 45–90 min at boiling point. After the reaction was over, the mixture was cooled, acidified with hydrochloric acid and extracted with ether. The organic layer was washed with water and acids were re-extracted into 5% sodium bicarbonate solution. The alkaline solution of sodium salts was acidified to pH 6 with acetic acid. The precipitated *E*-isomer was filtered off and recrystallized from methanol (yield 34–88%). To the filtrate hydrochloric acid was added, and an additional crystalline crop consisting of corresponding *Z*-isomer was filtered off and recrystallized from benzene/petroleum ether (yield 1–18%). Data for prepared acids are listed in Tables 2–4.

Irradiation of (E) - 2 - (4 - *tolyl*) - 3 - (2 - *furyl*)*acrylic acid* (**1**)

A solution of acid **1** (4.0 g, 17.5 mmole) in benzene (2.0 l.) was irradiated with pyrex filtered light of the mercury arc lamp for 48 hr at room temperature. Air was bubbled through the solution. During the irradiation, a pale yellow deposit was formed and was scraped off the irradiation wall surface from time to time. The deposit (0.4 g) consisted mainly of polymers and was not studied further. Filtered solution of photoproduct was evaporated under reduced pressure. The dark oily residue was triturated with 5% sodium carbonate solution to separate acidic component. Alkaline solution (Na salt of **16**) was acidified with 10% hydrochloric acid yielding 5-methyl-naphtho[2,1-*b*]furan-8-carboxylic acid (**16**) which was recrystallized from glacial acetic acid (1.4 g, 35%), m.p. 240–245°. UV: λ_{max} (log ϵ) = 315 nm (4.00), 236 nm (4.55), 200 nm (3.94). IR: $\nu_{C=O}$ 1660 cm^{-1}. ^1H NMR$_{(CF_3COOH)}$: $\delta = 2.55$ (CH_3, s); 7.4–9.1 (5H, m, naphthofuran ring). MS: *m*/*e* = 226 (100%, M^{+}), 209 (30), 181 (20), 153 (15), 152 (15). ($C_{14}H_9O_3$ requires: C, 74.33; H, 4.45. Found: C, 74.27; H, 4.17%).

The residue after trituration with sodium carbonate was recrystallized from methanol and crystalline 6 - (4 - tolyl) - 2,3 - epoxy - 2,3 - dihydrofuro[3,2 - *b*]pyran - 5 - one (**17**) (30%, m.p. 160–162°) was obtained. UV: λ_{max} (log ϵ) = 284 nm (4.02), 220 nm (4.20), 202 nm (4.34). IR: $\nu_{C=O}$ = 1745 cm^{-1}. ^1H NMR (Me_2CO-d_6): $\delta = 2.34$ (CH_3, s); 6.34 (1H, d, J = 5 Hz) and 7.42 (1H, d, J = 5 Hz) for epoxide ring protons; 7.45 (1H, s) vinylic proton at C_7; 7.03 (2H) and 7.57 (2H) an A_2B_2 system J = 8 Hz for p-substituted phenyl. MS: *m*/*e* = 242 (M^{+}, 100%), 170 (20), 116 (32), 115 (44), 82 (65). ($C_{14}H_{10}O_4$ requires: C, 69.42; H, 4.16. Found: C, 69.78; H, 4.46%).

Irradiation of (E) - 2 - (3 - *methoxyphenyl*) - 3 - (2 - *furyl*) *acrylic acid* (**4**)

A solution of acid **4** (4.0 g, 16.4 mmole) in benzene (2.0 l.) was irradiated in a "Rayonet" photochemical reactor equipped with 16 (21 W, 300 nm) UV lamps. The progress of reaction was monitored by UV. The irradiation under aeration was continued for 120 hr and solution evaporated. The residue was recrystallized from acetic acid yielding 2.0 g (50%) of crystalline 6-methoxynaphtho[2,1-*b*]furan-8-carboxylic acid (**18**), m.p. 241°. UV: λ_{max} (log ϵ) = 304 nm (4.02), 294 nm (4.59), 232 nm (4.59). IR: $\nu_{C=O}$ = 1670 cm^{-1}. ^1H NMR (CF_3COOH): $\delta = 4.15$ (OCH_3, 3H, s); 7.2–8.8 (naphthofuran ring, 6H, m). MS: *m*/*e* = 242 (M^{+}, 100%), 199 (40), 155 (7), 154 (8), 126 (12), 116 (20). ($C_{14}H_{10}O_4$ requires: C, 69.42; H, 4.16. Found: C, 69.13; H, 4.58%).

Irradiation of (E) - 2 - (4 - *chlorophenyl*) - 3 - (2 - *furyl*)*acrylic acid* (**5**)

A solution of acid **5** (4.0 g, 16 mmole) in benzene (2.0 l.) was irradiated by pyrex filtered mercury arc light for 48 hr, with aeration of the reaction mixture. After evaporation the oily residue was triturated with 5% sodium carbonate. On acidification alkaline solution yielded 1.2 g (30%) of starting compound (**5**). The residue after trituration was thoroughly washed to remove sodium carbonate traces and recrystallized from methanol. Crystalline 6 - (4 - chlorophenyl) - 2,3 - epoxy - 2,3 - dihydrofuro[3,2 - *b*]pyran - 5 - one (**19**) (0.6 g, 15%) melting at 133–135° was obtained. UV: λ_{max} ($\log \epsilon$) = 278 nm (3.89), 245 nm (3.83), 223 nm (4.05). IR: $\nu_{C=O} = 1745\ cm^{-1}$.$^1H$ NMR ($Me_2CO–d_6$): $\delta = 6.62$ (1H, d, J = 6 Hz) and 7.75 (1H, d, J = 6 Hz) for epoxyde ring protons; 7.4–8.1 (5H, m) for p-substituted phenyl and vinylic protons at C_7. MS: *m*/*e* = 264 ($M^{\dot{+}}$, 8%) and 262 ($M^{\dot{+}}$, 20%), 227 (30), 190 (20), 161 (17), 138 (34), 136 (100), 101 (40), 84 (55), 82 (92), 78 (8), 75 (30), 54 (40). ($C_{13}H_7ClO_4$ requires: C, 58.95; H, 3.40. Found: C, 58.58; H, 3.38%).

Irradiation of (E) - 2 - (3 - *tolyl*) - 3 - (5 - *methyl* - 2 - *furyl*) - *acrylic acid* (**9**)

The solution of acid **9** (4.0 g, 16.5 mmole) in benzene (2.0 l.) was irradiated as above during 48 hr. Solvent was evaporated, the residue was triturated with 5% sodium carbonate and recrystallized from methanol. 7a - Hydroxy - 2 - methyl - 6 - (3 - tolyl) - 3a,7a - dihydrofuro[3,2 - *b*]pyran - 5 - one (**21**) (1.7 g, 40%), m.p. 124–126° was obtained. UV: λ_{max} ($\log \epsilon$) = 273 nm (4.03), 223 nm (4.06), 213 nm (4.55). IR: $\nu_{C=O}$ 1765 cm^{-1}. ^1H NMR ($Me_2CO–d_6$): $\delta = 1.58$ (CH_3, s); 2.36 (tolyl–CH_3, s); 6.17 and 6.35 (2H, J_{AB} = 5.4 Hz) for protons at C_3 and C_{3a}; 7.2–7.8 (5H, m) for m-substituted phenyl and vinylic proton at C_7; 10.99 (1H, s, D_2O exch.) for OH at C_{7a}. MS: *m*/*e* = 258 ($M^{\dot{+}}$, less than 5%), 242 (13), 241 (52), 116 (18), 115 (33), 98 (12), 97 (90), 82 (17), 69 (20), 43 (100%). ($C_{15}H_{14}O_4$ requires: C, 69.76; H, 5.42. Found: C, 69.44; H, 5.90%).

Irradiation of (E) - 2 - (4 - *chlorophenyl*) - 3 - (5 - *methyl* - 2 - *furyl*)*acrylic acid* (**12**)

The benzene solution of acid **12** (4.0 g, 15.3 mmole) was irradiated with pyrex filtered UV light for 48 hr in aerobic conditions. Unreacted **12** (0.4 g, 10%) was removed by trituration with sodium carbonate solution, and the residue was recrystallized from methanol. 7a - Hydroxy - 2 - methyl - 6 - (4 - chlorophenyl) - 3a,7a - dihydrofuro[3,2 - *b*]pyran - 5 - one (**22**) (2.4 g, 60%) m.p. 138–140° was obtained. UV: λ_{max} ($\log \epsilon$) = 274 nm (4.01), 222 nm (4.05), 200 nm (4.20). IR: $\nu_{C=O}$ 1750 cm^{-1}. ^1H NMR ($Me_2CO–d_6$): $\delta = 1.59$ (CH_3, s); 6.21 and 6.39 (2H, J_{AB} = 5.4 Hz) for protons at C_3 and C_{3a}; 7.50 (2H) and 7.98 (2H) an A_2B_2 system, J = 8.6 Hz for p-substituted phenyl; 7.63 (1H, s) for vinylic proton at C_7; 11.03 (1H, s, D_2O exch.) for OH at C_{7a}. MS: *m*/*e* 280 and 278 ($M^{\dot{+}}$, low intensity), 264 (20%), 263 (29), 262 (20), 261 (80), 205 (20), 138 (13), 136 (40), 101 (19), 98 (20), 97 (80), 82 (30), 75 (15), 69 (26), 51 (15), 42 (100). ($C_{14}H_{11}ClO_4$ requires: C, 60.30; H, 3.94. Found: C, 59.98; H, 4.02%).

Irradiation of (E) - 2 - (4 - *methoxyphenyl*) - 3 - (5 - *methyl* - 2 - *furyl*)*acrylic acid* (**10**)

Without sensitizer. Starting compound **10** (4.0 g, 15.5 mmole) in benzene (2.0 l.) was irradiated with pyrex filtered mercury arc lamp for 48 hr under air at room temperature. After evaporation of solvent photoproduct was recrystallized from methanol yielding 1.9 g (48%) 7a - hydroperoxy - 2 - methyl - 6 - (4 - methoxyphenyl) - 3a,7a - dihydrofuro[3,2 - *b*]pyran - 5 - one (**23**) m.p. 164–165°. UV: λ_{max} ($\log \epsilon$) = 304 nm (4.02), 287 nm (3.99), 227 nm (4.05). IR: $\nu_{C=O}$ 1760 cm^{-1}. ^1H NMR ($Me_2CO–d_6$): $\delta = 1.53$ (CH_3, s); 3.80 (OCH_3, s); 6.15 and 6.28 (2H, J_{AB} = 6 Hz) for protons at C_3 and C_{3a}; 6.98 (2H) and 7.90 (2H) an A_2B_2 system, J = 10 Hz, for p-substituted phenyl; 7.42 (1H, s) for vinylic proton at C_7; 10.92 (1H, s, D_2O exch.) for OOH at C_{7a}. MS: *m*/*e* 290 ($M^{\dot{+}}$, 26%), 274 (6), 258 (25), 257 (46), 201 (45), 186 (20), 133 (8), 131 (8), 132 (53), 98 (10), 117 (19), 97 (100), 89 (35), 43 (57), 69 (18), 63 (18). ($C_{15}H_{14}O_6$ requires: C, 62.06; H, 4.82. Found: C, 62.07; H, 4.69%).

An unsensitized irradiation experiment was repeated under the same conditions but with methanolic solution. From **10** (4.0 g; 15.5 mmole) in methanol (750 ml) 1.8 g (45%) of recrystallized photoproduct **23** was obtained.

With sensitizer. The irradiation was carried out with 4.0 g (15.5 mmole) of **10** in methanol (750 ml) in a presence of 0.2 g Bengal Rose as sensitizer. The reaction was monitored by UV spectra. After 20 hr of irradiation at 254 nm (Rayonet reactor) and elaboration of product as above, 2.8 g (70%) of crystalline product was obtained. The product has proved to be identical with a sample of **23** obtained without sensitizer.

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