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CONVENIENT METHOD FOR THE SYNTHESIS OF SOME NEW 2-(2-CARBOXYSTYRYL)-5-(2-METHOXYCARBONYLSTYRYL) FURANS

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Abstract — It is described very convenient method for the synthesis of some 2-(2-carboxystyryl)-5-(2-methoxycarbonylstyryl) furans. The configuration on the both ethene chain is "E".

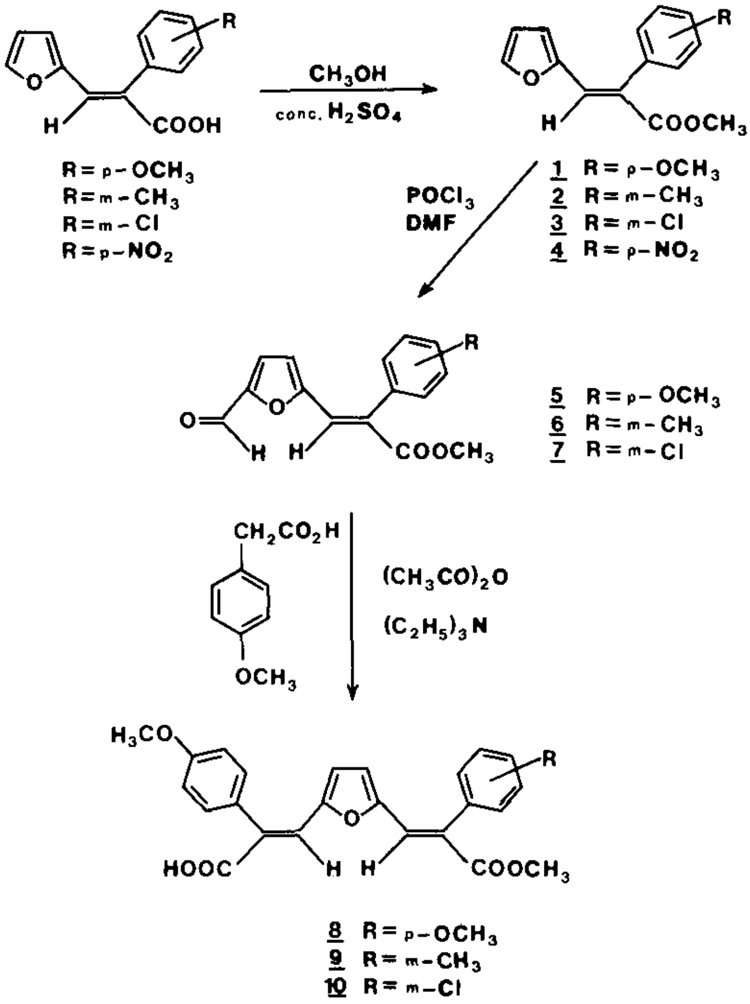
Our continuing interest in the synthesis and photochemistry of heterocyclic acrylic acids[1,2,3] prompted us to develop the new synthetic method for preparation of unsymetrical 2,5-distyrylfurans, substituted with carboxy and methoxycarbonyl group in the ethene chains.

The presence of the carboxy group on the ethene chain which is attached in the position 2 of the furan nuclei and the methoxycarbonyl group on the ethene chain which is attached in the position 5 of the furan nuclei open the posibility of examination of two types of photochemical reactions at the same time and on the same molecule; lactonization and/or dehydrocyclization reaction. Therefore we synthesized the title compounds starting from some before reported 3-(2-furyl)-2-arylacrylic acids[1], following their esterification, formylation of the furan nuclei in the position 5 and Oglialoro condensation with substituted phenylacetic acids.

It can be pointed out that the introduction of the formyl group in the position 5 of the furan nuclei in the methyl esters of 3-(2-furyl)-2-(substituted phenyl)acrylic acids was more successful than the formylation of the corresponding 1-phenyl-2-(2-thienyl)ethene[3] or 1-phenyl-2-(2-furyl)ethene[4]. The presence of methoxycarbonyl group which is in the conjugation with furan nuclei strongly influence the introduction of the formyl group.

On the other hand, the different substituents on the phenyl nuclei either in the position m- or p- do not influence strongly the formylation process except the p-NO_2 substituent which depress formylation.

The configuration on the both ethene chain is "E".



EXPERIMENTAL

IR spectra were obtained with a Perkin Elmers 257 spectrometer. NMR spectra were recorded on a Varian T-60 or Joel J.M.M.-FX 100 FT spectrometer with tetramethylsilane as the internal reference.

Starting materials E-3-(2-furyl)-2-(substituted phenyl)acrylic acids were prepared by published procedures.[1]

General Procedure for the Preparation of E-Methyl-3-(2-furyl)-(2-substituted phenyl)acrylates

All methyl esters were prepared by the known method[5] by 3 hours heating of (0.01 mol) the corresponding acrylic acid dissolved in ca 50 ml of absolute methanol in which was added 1/2 ml of conc. H_2SO_4. The cooled solution was poured into the 200 g of ice and crystallized esters were filtered off and recrystallized from methanol. The yields were 65-80%.

TABLE I. Physical and Spectral Data of Methyl Esters[a]

Cmpd	Yield %	Mp ^{o}C	Ir (KBr) $\nu_{C=O}$, $\nu_{C=C}$	^{1}H NMR (δ)
1	80	63	1720, 1600	7.69 (s, 1H, ethylenic), 7.3-6.9 (m, 5H), 6.25 (q, 1H, J=1.8 Hz), 5.84 (d, 1H, J=3.6 Hz), 3.85 (s, 1H, OCH_3), 3.76 (s, 1H, OCH_3),
2	65	84	1720, 1600	7.71 (s, 1H, ethylenic), 7.4-7.00(m, 5H), 6.21 (q, 1H, J=1.8 Hz), 5.74 (d, 1H, J=3.6 Hz), 3.74 (s, 3H, OCH_3), 2.35 (s, 3H, CH_3),
3	58	58	1720, 1600	7.71 (s, 1H, ethylenic), 7.39-7.06 (m, 5H), 6.29 (q, 1H, J=1.8 Hz), 5.93 (d, 1H, J=3.6 Hz), 3.94 (s, 3H, OCH_3),
4	76	77	1700	8.2 (s, 1H, ethylenic), 7.9-7.6 (m, 5H), 7.24 (d, 1H, J=3.6 Hz), 6.59 (q, 1H, J=1.8 Hz), 3.94 (s, 1H, OCH_3).

(a) All compounds gave correct elemental analysis.

General Procedure for the Preparation of E-Methyl 3-(5-Formyl-2-furyl)-2-(substituted phenyl)acrylates[a]

The corresponding methyl esters of the furylphenylacrylic acids were formylated by Vilsmeier formylation[6].

Phosphorus oxychloride (4 ml) was added dropwise with cooling to a mixture of methyl esters (0.01 mole) and dimethylformamide (3 g). The apparatus being protected with a calcium chloride tube. The mixture was heated to 90-100 °C for 3 h, then cooled and poured onto crushed ice (50 g). The resulting mixture was made weakly alkaline with sodium hydroxide. The solid was filtered off, washed with water and recrystallized from methanol to give formylated products. The yields are 21-91%.

TABLE II. Physical and Spectral Data of Formylated Methyl Esters[a]

Cmpd	Yield %	Mp ^{o}C	Ir, C=O ester, C=O aldehyde, C=C	^{1}H NMR (δ)
5	91	83	1720, 1670, 1620	9.76 (s, 1H, $C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$), 7.71 (s, H, ethylenic), 7.26-6.91 (m, 5H), 5.84 (d, 1H, J=3.6 Hz), 3.85 (s, 1H, OCH_3), 3.76 (s, 1H, OCH_3),
6	68	124-126	1720, 1670, 1620	9.56 (s, 1H, $C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$), 7.74 (s, 1H, ethylenic), 7.28-7.05 (m, 4H), 6.77 (d, 1H, J=3.8 Hz), 3.80 (s, 3H, OCH_3), 2.38 (s, 3H, CH_3),
7	70	136-137	1720, 1670, 1620	9.55 (s, 1H, $C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$), 7.76 (s, 1H, ethylenic), 7.45-7.27 (m, 4H), 7.05 (d, 1H, J=3.8 Hz), 6.92 (d, 1H, J=3.8 Hz), 3.81 (s, 3H, OCH_3).

(a) All compounds gave correct elemental analysis.

General Procedure for the Preparation of 2-[2-(p-Methoxyphenyl)-2-carboxy-1-ethenyl]-5-[2-(substituted phenyl)-2-methoxycarbonyl-1-ethenyl]furans[a]

The title compounds were prepared from formylated esters (0.01 mole) and p-methoxyphenylacetic acid (0.01 mole) in a mixture of triethylamine (10 ml) and acetic anhydride (10 ml) heating the mixture for 1.5-2 h 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. The yields are 40-85%.

TABLE III. Physical and Spectral Data of 2,5-Disubstituted Furans[a]

Cmpd	Yield %	Mp °C	Ir, C=0 ester, C=0 acid, C=C ethylene, C=C	^{1}H NMR (δ)
8	85	235	1720, 1670, 1620, 1600	7.49 (s, 1H, ethylenic), 7.45 (s, 1H, ethylenic), 9.2-6.9 (m, 8H), 5.77 (s, 2H), 3.83 (s, 6H, OCH_3), 3.71 (s, 3H, OCH_3),
9	55	163-164	1720, 1670, 1620, 1600	7.47 (s, 2H, ethylenic), 7.23-7.00 (m, 8H), 6.94 (d, 1H, J=3.8 Hz), 6.89 (d, 1H, J=3.8 Hz), 3.82 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 2.33 (s, 3H, CH_3),
10	40	196-199	1720, 1670, 1620, 1600	8.02 (s, 2H, ethylenic), 7.52-6.92 (m, 8H), 5.98 (d, 1H, J=3.8 Hz), 5.76 (d, 1H, J=3.8 Hz), 3.83 (s, 1H, OCH_3), 3.73 (s, 1H, OCH_3).

(a) All compounds gave correct elemental analysis.

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