MONO- AND DIHALOGENOFURFURALS IN THE WITTIG REACTION

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The reaction of 3(5)-monohalogeno- and 4,5-dihalogenofurfurals with alkoxycarbonylmethylenetriphenylphosphoranes has given esters of β-[3(5)-mono- and -4,5-dihalogeno-2-furyl]-acrylic acids, which are converted by alkaline hydrolysis into the corresponding halogen-substituted furylacrylic acids.

The behavior of carbonyl compounds of the heterocyclic series, and especially furan aldehydes, in the Wittig reaction has been studied inadequately [1]. Recently, the syntheses of ethyl esters of α-bromo-β-[5-nitro(halogeno)-2-furyl]acrylic acids with the aid of the Wittig reaction of 5-iodo- and 5-nitrofurfurals with ethoxycarbonylbromomethylenetriphenylphosphorane have been described [2, 3]. A series of patents devoted to the synthesis of 2-(5-nitro-2-furyl)vinyl derivatives from 5-nitro-, 5-iodo-, and 5-ethoxycarbonylfurfurals is also known [4, 5].

It appeared of interest to study the behavior of other halogen-substituted furfurals in the Wittig reaction with resonance-stabilized phosphoranes, all the more because, for example, the synthesis of (4,5-dibromo-2-furyl)acrylic acid by the Perkin or Knoevenagel reaction [6] has proved impossible, since the initial 4,5-dibromofurfural readily resinifies under the reaction conditions.

It has been shown that 4,5-dihalogenofurfurals, like the 5- or 3-monohalogenofurfurals, readily react with alkoxycarbonylmethylenetriphenylphosphoranes forming the corresponding esters of mono- and dihalogenofurylacrylic acids with yields of up to 80% (Table 1).

The hydrolysis of the esters of halogen-substituted furylacrylic acid obtained leads smoothly to the formation of the corresponding furylacrylic acids. In view of the high reactivity of bromine in the carbonyl derivatives of 4,5-dibromofuran, the hydrolysis of esters of 4,5-dibromo-2-furylacrylic acid was performed under mild conditions, giving the completely stable 4,5-dibromofurylacrylic acid.

EXPERIMENTAL

The UV spectra were taken in methanol on an SF-4A spectrophotometer and the IR spectra in paraffin oil on a UR-20 instrument.

General Method of Synthesizing the Esters of 3(5)-Mono- and 4,5-Dihalogenofurylacrylic Acids (I-IX). A solution of 5 mmoles of the appropriate substituted furan aldehyde and 5 mmoles of alkoxycarbonylmethylenetriphenylphosphorane in 10 ml of benzene was boiled for 8-12 h, the course of the reaction being monitored by thin-layer chromatography in a nonfixed layer of alumina. After the end of the reaction, the benzene was distilled off, the residue was dissolved in ether, and the esters of halogen-substituted furylacrylic acids that had been formed were separated from the triphenylphosphine oxide by chromatographing the reaction mixture on alumina of activity grade III in ether, the first portions of the eluate being collected.

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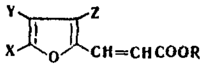
TABLE 1. β-(Halogeno-2-furyl)acrylic Acids and Their Esters



Compound	X	Y	Z	R	Mp, °C	Empirical formula	Found, %			Calculated, %			UV spectra		IR spectra			Yield, %
							C	H	halogen	C	H	halogen	λ_{max}, nm	lg ε	$\nu_{C=C}$	$\nu_{\mathrm{C}\langle^{\mathrm{O}}_{\mathrm{OR}}}$	ν_{C-O-C}	
I	Br	Br	H	CH_3	98—99	$C_8H_6Br_2O_3$	31,4	2,3	51,4	31,0	2,0	51,6	312	4,39	1650	1725	1178 1255	64
II	Br	Br	H	C_2H_5	74—75	$C_9H_8Br_2O_3$	34,2	2,6	47,5	33,4	2,5	49,3	312	4,43	1640	1724	1166 1260	60
III	I	Br	H	CH_3	119—120	$C_8H_6BrIO_3$	26,2	1,9	58,2	26,9	1,7	57,9	322	4,37	1647	1713	1177 1269	67
IV*	I	Br	H	C_2H_5	104—105	$C_9H_8BrIO_3$	28,8	2,5	55,9	29,1	2,2	55,7	321	4,01	1645	1710	1170 1256	63
V*	Br	H	H	CH_3	62	$C_8H_7BrO_3$	—	—	34,1	—	—	34,6	—	—	—	—	—	80
VI*	Br	H	H	C_2H_5	41—42	$C_9H_9BrO_3$	—	—	—	—	—	—	310	4,35	1650	1730	—	78
VII*	I	H	H	CH_3	81—82	$C_8H_7IO_3$	—	—	45,4	—	—	45,3	315	4,23	1650	1720	—	68
VIII*	I	H	H	C_2H_5	61—62	$C_9H_9IO_3$	—	—	43,1	—	—	43,5	317	4,46	1640	1700	—	64
IX	H	H	Br	CH_3	66,5—67,5	$C_8H_7BrO_3$	41,8	3,2	34,2	41,6	3,0	34,6	305	4,01	1625 1640	1679	—	68
X	Br	Br	H	H	242	$C_7H_4Br_2O_3$	28,8	1,6	54,1	28,4	1,4	54,0	298	4,29	—	—	ν_{OH} 2600	82
XI	NO_2	H	Br	CH_3	116—117	$C_8H_6BrNO_5$†	34,69	2,5	28,9	34,8	2,2	29,0	—	—	—	—	—	70
XII*	I	Br	H	H	171—175	$C_7H_4BrIO_3$	—	—	—	—	—	—	339	4,37	1648 1618	1718	ν_{OH} 2518	78

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* Obtained by the Perkin reaction [7].

† Found, %: N 4.9. Calculated, %: N 5.1. The initial aldehyde was obtained by the nitration of 3-bromofurfural.

The solvent was distilled off, and the residue consisted of the esters of the corresponding mono- and dihalogen-substituted furylacrylic acids.

The yields, melting points, and spectral characteristics of the compounds obtained are given in Table 1.

4,5-Dibromofurylacrylic Acid (X). A solution of 0.47 g (1.5 mmole) of the ester (I) in 5 ml of 15% caustic soda solution was left overnight. Then the solvent was evaporated off by pouring the mixture into a Petri dish, after which the residue was dissolved in water and the solution was filtered and acidified with dilute hydrochloric acid. The acid (X) that precipitated was filtered off, dried, and crystallized from ethanol (Table 1).

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