

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $(\text{CD}_3)_2\text{CO}$ were measured with a Tesla PPR spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were recorded with an MS-902 apparatus (Jynni AEI). The dipole moments in benzene were determined. The measured concentrations of the solutions ranged from 0.0005 to 0.003 mole fraction. The IR spectra were recorded with a UR-20 spectrometer. The UV spectra of ethanol solutions of the compounds ($5 \cdot 10^{-4}$ – $1 \cdot 10^{-5}$ M) were recorded with a Specord UV-vis spectrophotometer. Chromatography was carried out on a loose thin layer of Al_2O_3 (activity II) with elution by benzene–chloroform (1:1).

1-Diethylamino-2-(5'-nitro-2'-furyl)ethylene (II). A 1.46 g (0.02 mole) sample of diethylamine was added to a solution of 2.18 g (0.01 mole) of 1-bromo-2-(5'-nitro-2'-furyl)ethylene (I) in 50 ml of absolute acetone (benzene), and the resulting solution was allowed to stand at room temperature for 1–2 days. The precipitated diethylamine hydrobromide was separated, the filtrate was vacuum evaporated, and the residue was crystallized twice from heptane to give 1.9 g (40%) of red-violet crystals of II with mp 63–65°C.

The characteristics and yields of enamines II–XII are presented in Table 1. In some cases the enamines were purified by reprecipitation from benzene solution by the addition of ether.

1-(5'-Nitro-2'-vinylfuryl)pyridinium Bromide (XIII). A solution of 2.18 g (0.01 mole) of I in 20 ml of pyridine was refluxed for 20 h, after which the excess pyridine was removed in vacuo, and ethanol was added to the residue. The solution was refluxed with activated charcoal, ether was added, and the resulting precipitate was separated to give 2.5 g (85%) of yellow-white crystals with mp 217°C (from alcohol).

Quaternary salts XIV and XV are similarly obtained (Table 1).

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SYNTHESIS OF β -(4,5-DIHALOFURYL)ACRYLIC AND -PROPIOLIC ACIDS

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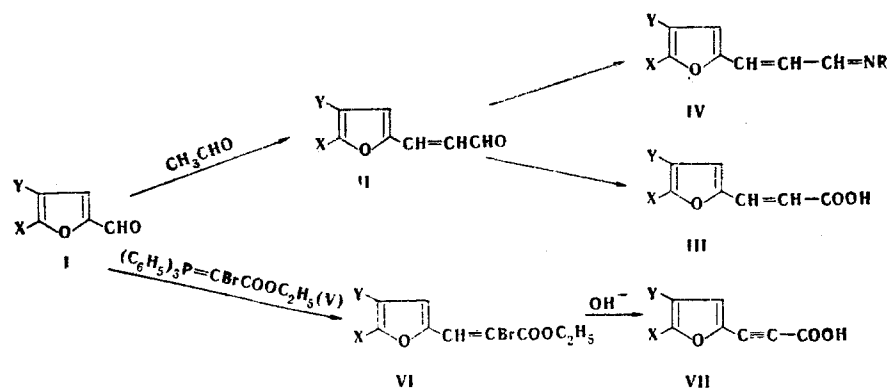
Reaction of 4,5-dihalofurfurals with acetaldehyde and with carbethoxybromomethylene-phosphorane gave, respectively, 4,5-dihalofurylacroleins and β -(4,5-dihalo-2-furyl)- α -bromoacrylic acid esters. The latter were converted to 4,5-dihalo-2-furylpropiolic acids by the action of alkali.

It is known that unsaturated furan-2-carboxylic acids have antimicrobial and fungistatic activity [1, 2]. In this connection it seemed of interest to accomplish the synthesis of unsaturated 4,5-dihalofurancarboxylic acids from 4,5-dihalofurfurals. Some β -(4,5-dihalofuryl)-2-acrylic acids have been previously obtained via the Wittig reaction [3]. The synthesis of these acids by condensation of 4,5-dihalofurfurals with acetaldehyde and subsequent oxidation of the resulting furylacroleins to furylacrylic acids seemed to be a promising method.

We established that the reaction of 4,5-dibromo- and 4-bromo-5-iodofurfurals (Ia,b) with acetaldehyde in the presence of sodium hydroxide gives the rather stable 4,5-dibromo-

and 4-bromo-5-iodofurylacroleins (IIa,b) for the confirmation of the structure of which we synthesized the oxime, semicarbazone, and thiosemicarbazone (IVa-c) of aldehyde IIa. However, oxidation of furylacroleins IIa,b with silver oxide gives β -(4,5-dihalo-furyl)-2-acrylic acids IIIa,b in low yields (see [3]).

The reaction of 4,5-dihalo-furfurals Ia, b with carbethoxybromomethylenetriphenylphosphorane (V) leads to β -(4,5-dihalo-2-furyl)- α -bromoacrylic acid esters VIa, b. The use of benzoic acid as a catalyst appreciably increases the reaction rate and the yields of esters VIa, b.



I-IV, VI, VII a X=Y=Br; b X=I, Y=Br; IV a R=OH; b R=NHCONH₂; c R=NHCSNH₂,

β -(4,5-Dibromo-2-furyl)propionic acid (VIIa) was obtained by dehydrohalogenation of ester VIa by the method in [4], whereas dehydrobromination with alcoholic KOH gives a difficult-to-separate mixture of β -(4,5-dibromo-2-furyl)- α -bromoacrylic acid and acid VIIa. However, propiolic acid VIIb was obtained in satisfactory yield from ester VIb under these conditions.

Attempts to accomplish the synthesis of 4,5-dihalo-2-ethynylfurans by decarboxylation of 2-furylpropionic acids VIIa,b were unsuccessful; resins were formed when these acids were steam distilled by the method in [5], heated in quinoline in the presence of copper sulfate [6], or subjected to thermal decarboxylation in vacuo by the method in [7].

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The IR spectra of mineral oil pastes of the crystalline compounds were recorded with a UR-20 spectrometer. The physical constants and yields of the synthesized compounds are presented in Table 1.

β -(4,5-Dihalo-2-furyl)acroleins (IIa, b). A 0.05 mole sample of 4,5-dihalo-furfural Ia, b was added at 0°C to 100 ml of 6% NaOH, after which a solution of 3.5 ml of acetaldehyde in 15 ml of water was added with stirring in the course of 1.5 h, and the mixture was allowed to stand for 45 min. The condensation product was removed by filtration, washed with water, and dried over calcium chloride. Compounds IVa-c were obtained by mixing alcohol solutions of IIa and the corresponding reagent; the resulting precipitate was removed by filtration and crystallized from alcohol. 2-Furylacroleins IIa,b were oxidized to acids IIIa, b with silver hydroxide by the method in [9].

Ethyl β -(4,5-dihalo-2-furyl)- α -bromoacrylates (VIa, b). A 0.03-mole sample of phosphorane V and 0.02 g of benzoic acid were added to a solution of 0.03 mole of Ia-b in 50 ml of warm benzene, and the mixture was allowed to stand at room temperature for 2 h. It was then refluxed for 8 h, during which the completion of the reaction was determined by means of thin-layer chromatography on Al₂O₃. The benzene was removed by distillation, and the residue was chromatographed on activity III Al₂O₃ [elution with diethyl ether-petroleum ether (2:1)]; ester VI was separated from the triphenylphosphine oxide in the first portions of the eluate.

4,5-Dibromo-2-furylpropionic Acid (VIIa). A mixture of 5 g (120 mmole) of the ester and a solution of 2.7 g (480 mmole) of KOH in 120 ml of water was refluxed for 1.5 h, after which it was cooled and acidified with dilute HCl, and the precipitate was removed by filtration.

4-Bromo-5-iodo-2-furylpropionic Acid (VIIb). A 0.45 g (10 mmole) sample of ester VIb was added to a solution of 0.22 g (40 mmole) of KOH in 10 ml of ethanol, and the mixture was allowed to stand overnight. The solvent was removed by distillation, and the residue

TABLE 1. Yields and Physical Constants of the Synthesized Compounds

Com- pound	mp, °C ^a	Found, %			Empirical formula	Calc., %			IR spec- trum, cm ⁻¹ ^b		Yield, %
		C	H	Br(I)		C	H	Br(I)	C=O	C=C	
IIa	129—130	29,7	1,3	57,5	C ₇ H ₄ Br ₂ O ₂	30,0	1,4	57,1	1670	1648	30
IIb	132—134	25,3	1,5	63,8	C ₇ H ₄ BrIO ₃	25,7	1,2	63,3	1683	1645	96
IIIa	242 ³	—	—	—	C ₇ H ₄ Br ₂ O ₃	—	—	—	1670	1620	2
IIIb	174—175 ⁸	—	—	—	C ₇ H ₄ BrIO ₃	—	—	—	—	—	6
IVa ^c	180	28,1	1,4	54,5	C ₇ H ₅ Br ₂ NO ₂	28,5	1,7	54,1	—	—	77
IVb ^c	210	28,8	2,0	47,9	C ₈ H ₇ Br ₂ N ₃ O ₂	28,5	2,1	47,5	—	—	86
IVc ^c	123—124	26,9	1,6	—	C ₈ H ₇ Br ₂ N ₃ OS	27,2	2,0	—	—	—	85
VIa	68—69	26,7	1,8	59,3	C ₉ H ₇ Br ₃ O ₃	26,8	1,7	59,4	1723	1620	63
VIb	85—86	23,9	1,7	64,0	C ₉ H ₇ Br ₂ IO ₃	24,0	1,6	63,8	1700	1610	64
VIIa	195	29,0	0,8	54,4	C ₇ H ₂ Br ₂ O ₃	28,6	0,7	54,4	1720	—	32
VIIb	190—192	24,5	0,9	60,4	C ₇ H ₂ BrIO ₃	24,6	0,6	60,7	1710	—	42

^aCompounds VII were crystallized from benzene-petroleum ether; the remaining compounds were crystallized from alcohol. ^bThe IR spectrum of VII contained a band at 2200 cm⁻¹ (C≡C). ^cFound for IVa-c: N 5.0, 12.7, and 12.0%. Calculated: N 4.7, 12.5, and 11.9%, respectively.

was dissolved in 20 ml of water, and the solution was worked up as in the preceding experiment

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