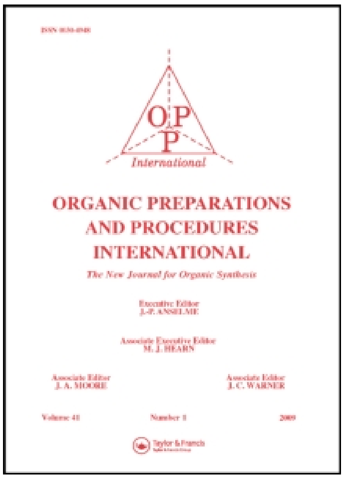

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NEW 5-SUBSTITUTED-2-FURALDEHYDES

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Distillation afforded 80 g. (86%) of 2-bromostyrene were collected at 50°C/2 mm Hg.

The figure shows the proton nmr spectrum of 2-bromostyrene in CCl_4. The chemical shifts are in δ ppm downfield from an external TMS. The two β protons appear as two sets of doublets between 5 and 5.7 ppm. The chemical shifts and the coupling constants are in agreement with those described by Gurudata et al.

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NEW 5-SUBSTITUTED-2-FURALDEHYDES

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The preparation of ten new 5-(substituted)-2-furaldehydes (Table I) are reported. 5-Aryl-2-furaldehydes (Compounds I & II, Table I) were prepared by reacting a diazotized solution of the corresponding aromatic amine with furfural and cupric chloride (Meerwein's arylation) according to the published procedure.[1] 5-Aryloxy-2-furaldehydes (Compounds III-VI) were obtained by the reaction of 5-bromo-2-furaldehyde with the corresponding phenols in dimethyl sulfoxide (DMSO) in the presence of sodium. 5-Arylsulfonyl-2-furaldehydes (Compounds VII-X) were synthesized by treatment of 5-bromo-2-furaldehyde with the appropriate sodium aryl sulfinate following the method of Benington *et al.*[2,5]

EXPERIMENTAL[3]

5-(3,4-Dimethoxyphenyl)-2-furaldehyde (I). General Procedure.- Veratrylamine[4] (30.6 g. 0.2 mole) was heated in water (40 ml) containing conc. HCl (29.5 ml) on a steam bath until a clear solution was obtained. An additional quantity of 60 ml. of conc. HCl was added and the solution was cooled to 0°. A solution of $NaNO_2$ (13.8 g. 0.2 mole) in water (80 ml) was then added dropwise with stirring at such a rate as to maintain the temperature below 5°. Stirring was continued for 0.5 hr at 5°. To this diazotized solution, furfural (19.2 g. 0.2 mole) in acetone (10 ml) and $CuCl_2 \cdot 2H_2O$ (3.92 g.) in water (60 ml) were added simultaneously dropwise with stirring. Stirring was continued at room temperature for an additional 12 hr period. The black tarry mass which had separated was thoroughly extracted with ether (4 x 250 ml) and the ethereal extract was washed with water and dried over anhydrous sodium sulfate. Removal of ether left a dark colored gummy mass which was dissolved in benzene and purified by passing over a column of silica gel. Elution with benzene yielded 5-(3,4-dimethoxyphenyl)-2-furaldehyde as yellow solid. Recrystallization from ether-petroleum ether (40-60°) afforded 16.2 g. (35%) of pure I as yellow needles, mp. 80°; IR (Nujol): 1680 cm^{-1} (C=O).

5-(3,4,5-Trimethoxyphenyl)-2-furaldehyde (II) was prepared similarly from 3,4,5-trimethoxyaniline.[5]

5-(4-Chlorophenoxy)-2-furaldehyde (III).- To a solution of *p*-Chlorophenol (12.85 g. 0.2 mole) in DMSO (125 ml) in a 250 ml round bottom flask

Table I. 5-Substituted-2-furaldehydes

Comp. No.	5-Substituent	Yield[a] (%)	mp.[b] (°C) (b.p/mm)	Formula	Analysis (Found)		
					C	H	N
I	3,4-Dimethoxyphenyl	35	80	$C_{13}H_{12}O_4$	67.23 (67.57)	5.17 (5.41)	
II	3,4,5-Trimethoxyphenol	45	118	$C_{14}H_{14}O_5$	64.12 (63.75)	5.34 (5.31)	
III	4-Chlorophenoxy	60	49-50	$C_{11}H_7ClO_3$	59.32 (59.41)	3.14 (3.51)	
IV	4-Nitrophenoxy	34	88-89	$C_{11}H_7NO_5$	56.65 (56.75)	3.00 (3.15)	6.01 (6.07)
V	6-Isopropyl-3-methylphenoxy (Thymoloxy)	49	(192-194/5)	$C_{15}H_{16}O_3$	73.77 (73.58)	6.55 (6.92)	
VI	4-Allyl-2-methoxyphenoxy (Eugenoloxy)	40	50	$C_{15}H_{14}O_4$	69.69 (69.77)	5.42 (5.58)	
VII	4-Chlorophenylsulfonyl	59	129	$C_{11}H_7ClO_4S$	48.79 (49.08)	2.58 (3.06)	
VIII	3,4-Dichlorophenylsulfonyl	41	115-116	$C_{11}H_6Cl_2O_4S$	43.28 (43.59)	1.96 (2.20)	
IX	4-Methylphenylsulfonyl	48	118-119	$C_{12}H_{10}O_4S$	57.61 (57.22)	4.00 (3.91)	
X	4-Methoxyphenylsulfonyl	59	152-154	$C_{12}H_{10}O_5S$	54.14 (53.68)	3.76 (3.90)	

(a) Yields are of the recrystallized products. (b) Compounds I & II were recrystallized from ether-pet.ether (40-60°), compounds III, IV & VI from ethyl acetate-pet.ether (40-60°) and compounds VII-X from $CHCl_3$-pet.ether (40-60°).

equipped with a $CaCl_2$ tube, was added freshly cut sodium (2.3 g. 0.1 mole) in small portions; the contents were warmed slightly. When the sodium completely reacted, 5-bromo-2-furaldehyde (17.5 g. 0.1 mole) was added in portions and the contents were heated on a steam bath for 4 hrs.

The reaction mixture was poured into water (250 ml) and steam distilled till no more unreacted 5-bromo-2-furaldehyde distilled over. The residue was extracted with ether (5 x 100 ml). The ethereal extract was washed with water, dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was recrystallized from ethyl acetate-petroleum ether (40-60°) to give 14 g. (60%) of 5-(4-chlorophenoxy)-2-furaldehyde as light yellow shiny needles, mp. 49-50°; Ir (Nujol): 1680 cm^{-1} (C=O).

Compounds IV-VI were prepared from the corresponding phenols by the same method.

5-(4-Methoxyphenylsulfonyl)-2-furaldehyde (X).- A mixture of 5-bromo-2-furaldehyde (17.5 g. 0.1 mole) and sodium 4-methoxyphenyl sulfinate[6] (19.4 g. 0.1 mole) in methyl cellosolve (150 ml) was heated to reflux for 1.5 hr. The cooled reaction mixture was poured into crushed ice and the solid that separated was collected with suction. It was washed thoroughly with water and dried. Recrystallization of the product from $CHCl_3$-pet. ether (40-60°) gave 15.7 g. (59%) of 5-(4-methoxyphenylsulfonyl)-2-furaldehyde as yellow crystalline solid, mp. 129°; Ir (Nujol): 1680 cm^{-1} (C=O), 1340 and 1160 cm^{-1} (SO_2). Compounds VII-IX were prepared similarly.

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