# MEERWEIN ARYLATIONS OF 2-FUROIC ACID AND METHYL 2-FUROATE

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#### Abstract

5-Aryl-2-furoic acids and their methyl esters have been prepared by Meerwein arylation. Spectroscopic (i.r. and u.v.) characteristics of the products are tabulated.

Meerwein arylations of 2-furoic acid were carried out in order to supplement the limited information in the literature.<sup>1,2</sup> Such a treatment of methyl 2-furoate does not appear to have been studied before.

Arylations of methyl 2-furoate in aqueous acetone with cupric chloride as catalyst afforded 5-substituted methyl 2-furoates together with small quantities of the corresponding acids formed by hydrolysis of the esters. The poor yields of some of the furoic esters obtained in the arylations could be due to the separation of methyl 2-furoate during the reaction. 5-o-Chlorophenyl-2-furoic acid decarboxylated at its melting point to a product identical with 2-o-chlorophenylfuran, b.p.  $90-92^{\circ}/0.7$  mm, obtained in 51 % yield by Johnson's method.<sup>3</sup> The bands in the region 650–1000 cm<sup>-1</sup> are difficult to assign definitely to C-H deformation modes of the benzene ring as the furans also give absorption peaks in this region.<sup>4,5</sup>

The carbonyl stretching frequency of 5-*p*-chlorophenyl-2-furoic acid was found to absorb at  $1667 \text{ cm}^{-1}$ . This suggests an intramolecular H-bridge which, however, must be unusual enough to warrant further study.

# Experimental

Analyses are by the Australian Microanalytical Service, Melbourne. Melting points were observed using a Gallenkamp apparatus and are uncorrected; boiling points are also uncorrected.

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<sup>1</sup> Rondestvedt, C. S., Jr, Org. React., 1960, 11, 189.

<sup>2</sup> Mathur, K. B. L., and Mehra, H. S., J. chem. Soc., 1961, 2576.

<sup>3</sup> Johnson, A. W., J. chem. Soc., 1946, 895.

- <sup>4</sup> Katritzky, A. R., and Ambler, A. P., in "Physical Methods in Heterocyclic Chemistry," (Ed. A. R. Katritzky) Vol. II, pp. 207, 312 (Academic Press: New York 1963).
- <sup>5</sup> Colthup, N. B., Daly, L. H., and Wiberly, S. E., "Introduction to Infrared and Raman Spectroscopy," pp. 248, 257 (Academic Press: New York 1964).

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# SHORT COMMUNICATIONS

Infrared spectra were recorded for the  $600-3500 \text{ cm}^{-1}$  region using a Perkin-Elmer doublebeam spectrophotometer 221. Solid samples were examined as mulls; Nujol and hexachlorobutadiene were used as mulling agents. Liquid samples were examined as thin films between plates. Ultraviolet spectra were recorded in methanol using a Perkin-Elmer 4000 Å Spectracord. The data obtained are given in Tables 1 and 2.

1					
1740–1715 (C=O str)	Infrared (cr 1300–1100 (ester C–O str)	Ultraviolet (nm) $\lambda_{\max} (\log \varepsilon)$			
1727br	1307, 1120	763			
1722	1298, 1130	982, 790, 760, 750	215 (4.02), 278 (4.08)		
1718-1710	1300, 1142	828, 805, 760, 738, 730, 675	213 (4.34), 296 (4.54)		
1738	1300, 1145	755	217 (4·31), 226 infl (4·12), 234sh (3·99), 297 (4·57)		
1718–1710	1302, 1140	790, 780, 752, 680	216 (4·16), 228 infl (3·87), 233sh (3·84), 298 (4·34), 312sh (4·25)		
1722	1295, 1135	830, 818, 800, 790, 752	218 (3.89), 304 (4.18)		
	1740–1715 (C=O str) 1727br 1722 1718–1710 1738 1718–1710 1722	Infrared (c 1740–1715 1300–1100 (C=O str) (ester C–O str) 1727br 1307, 1120 1722 1298, 1130 1718–1710 1300, 1142 1738 1300, 1145 1718–1710 1302, 1140 1722 1295, 1135	Infrared (cm <sup>-1</sup> )           1740-1715         1300-1100         1000-650           (C=O str)         (ester C-O str)         (C-H out-of-plane)           1727br         1307, 1120         763           1722         1298, 1130         982, 790, 760, 750           1718-1710         1300, 1142         828, 805, 760, 738, 730, 675           1738         1300, 1145         755           1718-1710         1302, 1140         790, 780, 752, 680           1722         1295, 1135         830, 818, 800, 790, 752		

	TABLE	1			
SPECTRA OF METHYL	5-ARYL-2-FUROATES	OBTAINED	IN	MEERWEIN	ARYLATIONS

<sup>a</sup> Liquid film.

TABLE 2

SPECTRA OF 5-ARYL-2-FUROIC ACIDS OBTAINED IN MEERWEIN ARYLATIONS

5-Aryl substituent	Infrared (cm) <sup>-1</sup> 2700-2500 1715-1680 1000-500 (OH str) <sup>a</sup> (C=O) (C-H out-of-plane)			Ultraviolet (nm) λ <sub>max</sub> (log ε)				
o-NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	2710, 2665, 2580	1700–1690br	852, 810, 780, 758, 742,	218 (4.03), 280 (4.14)				
$m-NO_2C_6H_5$	2667, 2564	1681	812, 805, 760, 738, 675	217 (4·23), 296 (4·21), 308sh (4·10)				
o-ClC <sub>6</sub> H <sub>5</sub>	2710-2650, 2580	1690–1680br	795, 758, 745	216 (4.05), 227sh (3.96), 235sh (3.91), 288sh (4.35), 295 (4.40), 319sh (4.22)				
m-ClC <sub>6</sub> H <sub>5</sub>	2730–2670, 2580	1692	784, 758, 686	216 • 5 (3 • 94), 228 infl (3 • 78), 234sh (3 • 69), 290sh (4 • 17), 297 (4 • 22), 312sh (4 • 09)				
p-ClC <sub>6</sub> H <sub>5</sub>	2660, 2570	1667	815, 805, 758	218 (3·82), 300 (4·20), 315sh (4·09)				

<sup>a</sup> All weak bands.

Organic extracts were dried with anhydrous magnesium sulphate. Unless otherwise stated light petroleum refers to fractions of b.p. 40–60°. Alumina (type H, Light and Co. Ltd) was used for adsorption chromatography.

Most of the starting materials were obtained commercially and used without purification. Methyl 2-furoate was prepared by the esterification of 2-furoic acid.<sup>6</sup> 5-p-Chlorophenyl-2-furoic acid, m.p. 191–193°, was prepared by the method of Mathur and Mehra.<sup>2</sup>

#### Meerwein Arylations

To 2-furoic acid (0.09 mol) in acetone (100 ml), filtered diazonium solution (prepared from 0.065 mol amine and cupric chloride (3 g) dissolved in water (4–5 ml)) was added at 20–30°. The mixture was stirred for 12 hr or longer and distilled in steam. The residue was extracted with ethyl acetate and the solution treated with charcoal and concentrated to initiate crystallization. Alternatively, the residue was extracted with ether from which the substituted furoic acid was isolated by

<sup>6</sup> Afrikian, V. G., and Grigorian, M. T., in "Syntheses of Heterocyclic Compounds," (Ed. A. L. Mndzhoian; transl. A. E. Stubbs) Vol. I, p. 27 (Consultant Bureau: New York 1959).

extraction with 5% aqueous sodium bicarbonate solution and subsequent acidification with hydrochloric acid. For the crystallization of the acids see Table 3.

	1						1		
Compound	Yield (%)	M.p. (°C)	Formula	Found (%)			Calc. (%)		
				С	н	N or Cl	C	н	N or Cl
5-Aryl-2-furoic acids									
o-Nitrophenyl <sup>a</sup>	46	223-224	$C_{11}H_7NO_5$	56.8	3.1	5.9	56.7	3.0	6.0
o-Chlorophenyl <sup>b</sup>	41	220-221 (dec.)	$C_{11}H_6ClO_3$	59.3	3.4	15.9	59.3	3 · 1	16.0
m-Chlorophenyl <sup>b</sup>	13	170-171	$C_{11}H_7ClO_3$	58.9	3.4	16.3	59.3	3.1	16.0
Methyl 5-aryl-2-furoates									
o-Nitrophenyl <sup>c,d</sup>	8	78–79	C <sub>12</sub> H <sub>9</sub> NO <sub>5</sub>	58.4	3.8	6.0	58.3	3.6	5.7
m-Nitrophenyl <sup>c,e</sup>	4	140-142	C12H9NO5	58.1	3.7	5.9	58.3	3.6	5.7
o-Chlorophenyl <sup>f,g</sup>	38.5	68-69	C <sub>12</sub> H <sub>9</sub> ClO <sub>3</sub>	60.7	4.0	15.2	60.9	3.8	15.0
m-Chlorophenyl <sup>h, i</sup>	10	81-82	C <sub>12</sub> H <sub>9</sub> ClO <sub>3</sub>	60.6	3.9	15.0	60.9	3.8	15.0
p-Chlorophenyl <sup>c, j</sup>	11	131-132	C12H9ClO3	60.6	3.9	14.8	60.9	3.8	15.0

 Table 3

 5-aryl-2-furgic acids and methyl esters from meerwein arylations

<sup>a</sup> Crystallized from ethyl acetate. <sup>b</sup> Crystallized from aqueous ethanol. <sup>c</sup> Crystallized from methanol. <sup>d</sup> 5-o-Nitrophenyl-2-furcic acid was obtained in 1% yield. <sup>c</sup> 5-m-Nitrophenyl-2-furcic acid was also obtained in 1% yield. <sup>f</sup> Crystallized from aqueous methanol. <sup>g</sup> 5-o-Chlorophenyl-2-furcic acid was also obtained in 1% yield together with some o-dichlorobenzene. <sup>h</sup> Crystallized from light petroleum. <sup>i</sup> B.p. 132-138<sup>o</sup>/0·4 mm; a small yield of 5-m-chlorophenyl-2-furcic acid was also obtained. <sup>J</sup> A small amount of 5-p-chlorophenyl-2-furcic acid was also obtained.

The same proportions were used for the arylation of methyl 2-furoate. When the sodium bicarbonate extracts of the steam distillate from the reaction mixture were acidified the carboxylic acids were found identical with those obtained by the arylation of 2-furoic acid.

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