SYNTHESIS OF 2-ARYL-3-FURANCARBOXYLIC ACIDS BY ARYLATION OF 3-FURANCARBOXYLIC ACID

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Arylation of 3-furancarboxylic acid (3-FCA) with 4-X-phenyldiazonium chlorides catalyzed by copper dichloride afforded the non-planar 2-(4-X-phenyl)-3-furancarboxylic acids (X = H, CH$_3$, OCH$_3$, Cl, Br, NO$_2$). Arylation of 3-FCA with 2-X-phenyldiazonium chlorides (X = COOCH$_3$, NO$_2$) yielded 2-(2-methoxycarbonylphenyl)-3-furancarboxylic acid and a 3 : 1 mixture of 2-(2-nitrophenyl)- and 5-(2-nitrophenyl)-3-furancarboxylic acids, respectively. The pK_a values of 2-(4-X-phenyl)-3-furancarboxylic acids linearly well correlate with the Hammett's σ_p^0 constants of substituents. The IR, UV, mass, and ^{13}C NMR spectra of the above-mentioned compounds are commented and the mechanism of arylation is discussed.

In contrast to 3-substituted derivatives, arylation of furan and its 2-X-substituted analogues (X = CH$_3$, CHO, COCH$_3$, COOH, COOR) has relatively been well investigated; it proceeds exclusively to α-position to give 5-arylfuran or its 2-X-substituted derivatives[1,2].

This paper deals with the synthesis and physicochemical properties of 2-aryl-3-furancarboxylic acids *I*. These compounds were obtained by arylation of 3-furancarboxylic acid[3] (3-FCA) in an aqueous acetone medium under catalysis of copper monochloride at a 1 : 1·5 ratio of 3-FCA to arenediazonium salt, and isolated via water-soluble salts.

This arylation proceeds under conditions of Meerwein–Müller radical reaction[4,5]; thus, the 4-substituted aryl radical selectively enters position 2 of the furan ring, i.e. in the neighbourhood of the relatively bulky COOH group leaving the two unoccupied positions intact. The aryl group is out of the furan ring plane, as evidenced by spectral measurements (Tables I to IV). Arylation with 2-X-substituted arenediazonium chlorides (X = COOCH$_3$, NO$_2$) furnished the corresponding 2-(2-methoxycarbonylphenyl)-3-furancarboxylic acid when X = COOCH$_3$, whilst a 3 : 1 mixture of 2-(2-nitrophenyl)-3-furancarboxylic (*A*) and 5-(2-nitrophenyl)-3-furancarboxylic (*B*) acids was obtained when X = NO$_2$ (Scheme 1). A considerable predominance of *A* over *B* backed the tendency of even the bulky 2-nitrophenyl radical to enter position 2 of the furan ring. The *A* : *B* ratio was deduced from the integrated intensi-

ties of the ^{1}H NMR spectra. Separation of this mixture of isomers on thin layers of silica gel afforded only 2-(2-nitrophenyl)-3-furancarboxylic acid in pure state, whereas the remaining 5-(2-nitrophenyl)-3-furancarboxylic acid always contained
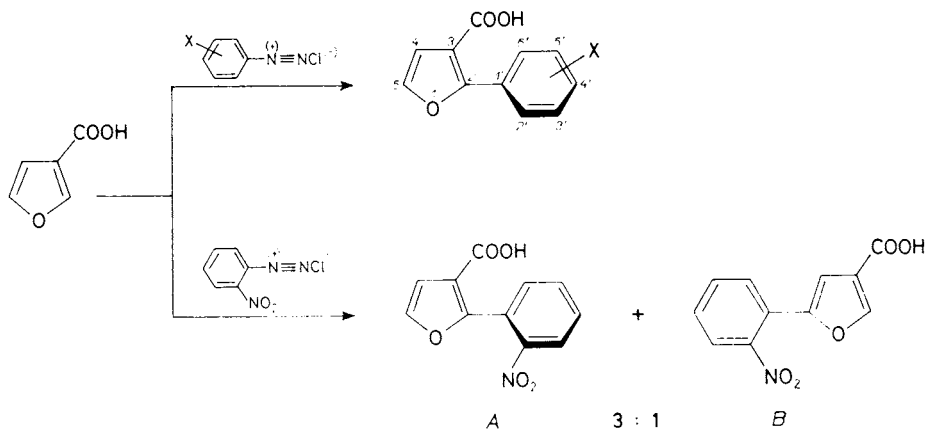
SCHEME 1

a small amount of the 2-substituted derivative *Ig*. Formation of the sole 2-(4-X--phenyl)-3-furancarboxylic acid can be explained by origination of a radical with an efficient delocalization of electrons to the adjacent carboxyl group after binding the aryl residue. These results show that the radical arylation proceeds to the opposite α-position of the furan ring contrary to electrophilic reactions of 3-FCA, as e.g. on nitration and bromination[6] (Scheme 2).
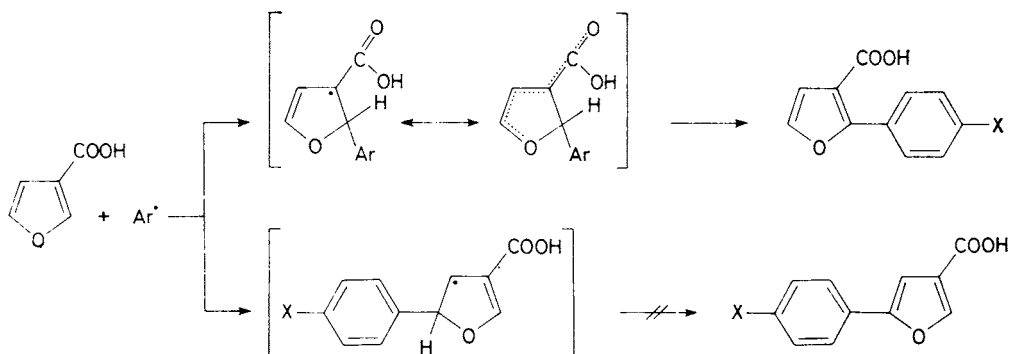
SCHEME 2

Physical constants and elemental analyses are listed in Table I; yields of this reaction are relatively low and vary within 10−30% of theory. It is noteworthy that other than arylated products were not found. The structure of all products was deduced from spectral data.

The common characteristic bands in the IR spectra (Table II) belong to the $\gamma(C—H)$ vibrations of the furan ring ($813 − 894\ cm^{-1}$), $\nu(COC)_{as}$ ($1\ 020 − 1\ 104\ cm^{-1}$, and $\nu(CO)$ of the carbonyl group ($1\ 680 − 1\ 691\ cm^{-1}$). The spectrum of 2-methoxycarbonyl derivative displayed two $\nu(CO)$ bands at $1\ 734$ and $1\ 680\ cm^{-1}$. The presence of an aromatic system evidenced the $\nu(=C—H)$ absorption at $1\ 473 − 1\ 520\ cm^{-1}$ and a relatively broad band at $2\ 660 − 3\ 253\ cm^{-1}$, overlapped by vibrations of an associated hydroxyl of the carbonyl group appearing at $3\ 200 − 3\ 660\ cm^{-1}$. Compounds Ib, Ic and Ih with a methyl group also reveal $\nu(C—H)$ bond vibrations at $2\ 481 − 2\ 730\ cm^{-1}$. Substances Id, Ie displayed $\nu(C—Hal)$ absorption at 686 to

TABLE I

2-(X-Phenyl)-3-furancarboxylic acids Ia—Ih

Compound	Formula M.w.	M.p., °C (Yield, %)	Calculated/Found	
			% C	% H
Ia H	$C_{11}H_8O_3$ (188·2)	148—152[a] (13·5)	70·21 70·29	4·28 4·39
Ib 4-CH$_3$	$C_{12}H_{10}O_3$ (202·2)	150—154[b] (12·5)	71·28 71·12	4·98 5·03
Ic 4-OCH$_3$	$C_{12}H_{10}O_4$ (218·2)	168—172[b] (10·5)	66·05 66·09	4·62 4·57
Id 4-Cl	$C_{11}H_7ClO_3$[c] (222·6)	165—168[b] (11·5)	59·35 59·41	3·17 3·21
Ie 4-Br	$C_{11}H_7BrO_3$[d] (267·1)	156—158[b] (15·0)	49·47 49·50	2·64 2·70
If 4-NO$_2$	$C_{11}H_7O_5N$[e] (233·2)	186—188[f] (36·5)	56·66 56·93	3·02 3·04
Ig 2-NO$_2$	$C_{11}H_7O_5N$[g] (233·2)	155—160[f] (22·0)	56·66 56·98	3·02 3·03
Ih 2-COOCH$_3$	$C_{13}H_{10}O_5$ (246·2)	130—134[a] (10·5)	63·42 63·41	4·06 4·01

[a] Crystallized from water; [b] crystalized from 50% methanol; [c] calculated: 15·93% Cl, found: 15·90% Cl; [d] calculated: 29·92% Br, found: 30·09% Br; [e] calculated: 6·01% N, found: 6·05% N; [f] crystallized from benzene; [g] calculated: 6·01% N, found: 6·09% N.

TABLE II

UV and IR spectral data of acids Ia—Ig

Compound	λ_{max}, nm (log ε, m^2 mol^{-1})			$\tilde{\nu}$, cm^{-1}					
				γ(C—H)	ν(COC)	ν(=CH)	ν(C=O)	ν(=CH)	ν(OH)$_{ass}$
Ia	211 (3·00)	217^a (2·96)	285 (2·95)	888	1 020 1 050	1 488	1 690	2 841—3 081	3 300—3 640
Ib^a	—	217^a (2·95)	290 (2·98)	890	1 021 1 068	1 505	1 691	2 802—3 081	3 400—3 660
Ic^b	210 (3·37)	—	300 (3·39)	890	1 028 1 069	1 504	1 691	2 761—3 061	3 380—3 640
Id^c	—	221^a (2·90)	293 (3·10)	889	1 017 1 066	1 486	1 689	2 816—3 086	3 200—3 500
Ic^d	207 (3·26)	222^a (3·05)	289 (3·25)	889	1 010 1 067	1 481	1 689	2 811—3 136	3 320—3 510
If^e	—	233 (2·68)	340 (2·92)	889	1 057 1 102	1 516	1 686	2 706—3 156	3 200—3 540
Ig^f	216 (3·28)	255 (3·22)	317^a (2·60)	886	1 033 1 057	1 520	1 680	2 760—3 100	3 260—3 580
Ih^g	205 (3·11)	222^a (3·00)	280 (2·60)	894	1 064 1 104	1 499	1 680 1 734	2 801—3 171	3 340—3 600

^{a} ν(CH) 2 481—2 701 cm^{-1}; ^{b} ν(CH) 2 510—2 780 cm^{-1}; ^{c} ν(C—Cl) 740 cm^{-1}; ^{d} ν(C—Br) 744 cm^{-1}; ^{e} ν(NO$_2$)$_{as}$ and ν(NO$_2$)$_s$ 1 576 and 1 341 cm^{-1}; ^{f} ν(NO$_2$)$_{as}$ and ν(NO$_2$)$_s$ 1 582 and 1 350 cm^{-1}; ^{g} ν(CH) 2 490—2 530 cm^{-1}.

TABLE III

^{1}H NMR data (δ, ppm) of acids $Ia—Ih$

Compound	pK_a	H-4	H-5 $J(4, 5)$	H-2' $J(2', 3')$	H-3'	Other signals
Ia	8·62	6·80 d	7·68 d 1·9	7·35— 7·89 m^b		
Ib	8·69	6·85 d	7·74 d 1·9	7·83 d 8·0	7·26 d	2·34 (CH$_3$)
Ic	8·67	6·75 d	7·68 d 1·9	7·86 d 9·0	6·96 d	3·77 s (OCH$_3$)
Id	8·62^a	6·83 d	7·68 d 1·9	8·06 d 8·5	7·48 d	
Ie	8·29	6·98 d	8·01 d 1·8	7·82 d 8·7	8·10 d	
If	7·79	6·88 d	7·91 d 1·8	8·12	8·65 m^b	
Ig	—	6·80 d	7·83 d 1·9	7·62	8·18 m^b	
Ih	—	6·73 d	7·70 d 1·9	7·49	7·93 m^b	3·60 s (COOCH$_3$)

^{a} The pK_a value at molar ionic strength $2 . 10^{-3}$; ^{b} protons of aromatic ring.

TABLE IV

^{13}C NMR data* (δ, ppm) of acids $Ia—Ig$

Compound	C-2	C-3	C-4	C-5	C-1'	C-2'	C-3'	C-4'	COOH	Other signals
Ia	155·9	114·5	113·3	142·4	129·4	128·2	129·3	128·0	164·4	
Ib	156·2	113·9	113·1	142·1	138·9	127·9	128·7	126·7	164·3	20·9 (CH$_3$)
Ic	156·6	122·2	113·2	141·3	128·5	129·8	113·8	160·2	164·5	55·4 (OCH$_3$)
Id	154·6	129·3	113·5	142·8	133·9	128·3	129·6	131·1	164·9	
Ie	154·5	115·4	113·5	142·7	128·6	129·8	131·2	122·6	164·4	
If	153·1	117·3	113·9	144·1	135·1	128·7	123·6	147·3	164·1	
Ig	152·3	116·1	112·0	144·0	124·2	148·3	124·5	130·9	163·5	133·2 132·5 (C-5') (C-6')

* ^1J(C-5, H-5) = 205·2 Hz, ^2J(C-3, H-4) = 10·4 Hz, ^1J(C-4, H-4) = 179·4 Hz, ^2J(C-4, H-5) = = 13·8 Hz.

776 cm^{-1}, nitro derivatives *If* and *Ig* also $v(NO_2)_s$ and $v(NO_2)_{as}$ absorptions at
1 341 − 1 586 cm^{-1}.

The UV spectra (Table II) are relatively simple with absorption bands appearing
at λ_{max} 285 − 340 nm, 217 − 274 nm and 205 − 216 nm, corresponding to $n \rightarrow \pi^*$
and $\pi \rightarrow \pi^*$ electronic transitions in furan and benzene rings, respectively. A band
of a great intensity at 285 − 340 nm is associated with electronic transitions of the
aryl residue. The UV spectra can be considered additive to some extent, as some
inflections due to electronic transitions of the furan ring[7] occured at 217 − 274 nm
in addition to the already mentioned band at 285 − 340 nm. This fact indicates that
the aryl moiety is out of the molecule plane and absorbs more or less individually;
a weak hypsochromic shift of the 2-methoxycarbonyl derivative is due to the presence
of COOCH$_3$ grouping in *o*-position of the phenyl ring.

Structures of all compounds described were backed by ^{1}H NMR spectra (Table III).
The H-5 proton signals resonate at lower field values within δ 7·68 − 8·01, those of
H-4 at higher one (δ 6·73 − 6·98). The conclusive evidence for the presence of an
aryl radical in position 2 of the furan ring in *Ia − Ih* are the doublets of H-4 and H-5,
with coupling constant $J(4, 5) = 1\cdot8 − 1\cdot9$ Hz. Providing the aryl radical enters posi-
tion 5 of the furan ring substituted in position 3, the coupling constant $J(2, 4)$ would
be 0·7 − 0·9 Hz (refs[8,9]). This particular case was observed with the reaction of
3-FCA a with 2-nitrobenzenediazonium chloride leading to a mixture of 2- and
5-arylated 3-furancarboxylic acids (Scheme 1). The ^{1}H NMR spectrum of this mix-
ture displayed doublets at δ 6·81 (H-4) and 7·84 (H-5), $J(4, 5) = 1\cdot9$ Hz, thus evi-
dencing the presence of a 2-substituted derivative. Doublets at δ 7·11 (H-4) and 8·38
(H-2), $J(2, 4) = 0\cdot9$ Hz prove the substitution at C-5.

The ^{13}C NMR spectra (Table IV) are in line with the proposed structures. For
compound *If* (X = 4-NO$_2$) both the decoupled and plane spectra were taken and
carbons were assigned according to direct $^1J(C, H)$ and $^2J(C, H)$ coupling constants.
The decoupled ^{13}C NMR spectrum possess 9 resonance signals: that at the lowest
magnetic field value was ascribed to the carbonyl carbon, that for C-2 appeared as
a broad multiplet. The doublet of doublets $^1J(C-5, H-5) = 205\cdot2$ Hz, $^2J(C-5, H-4) =$
$= 10\cdot4$ Hz belongs to C-5, that at δ 113·9, $^1J(C-4, H-4) = 179\cdot4$ Hz, $^2J(C-4, H-5) =$
$= 13\cdot8$ Hz to C-4. The $J(C, H)$ values, consistent with those reported[10] for 2- and
3-subsituted derivatives of furan, evidenced the arylation to proceed at C-2 of the
furan ring. The multiplet at δ 117·3 due to C-3 was overlapped by one peak of the
doublet of carbons C-3' and C-5'. The carbon signals for the phenyl group were
ascribed according to comparison of values calculated from additive contributions
with experimental data. Signals of carbon atoms for compounds *Ia − Ie* were deter-
mined employing the off-resonance technique. The decoupled ^{13}C NMR spectra
excepting that of *Ig* consisted of 9 signals, which were assigned according to the
effect of substituents of the benzene ring when contrasted with that of *If*. The plane
spectrum of *Ig* contained 11 resonance signals due to *o*-substituted benzene ring.

Common feature of all acompounds is the signal at δ 163·5 — 164·9, corresponding to the carbon of carboxyl group, and further ones at δ 112·0 — 113·9 (C-4) and 113·9 — 129·9 (C-3). The character of the substituent influenced not only, as anticipated, the chemical shift of C-2, but in a greater extent also that of C-5.

The electron impact mas spectra of $Ia - Ih$ showed three fragmentation pathways of molecular radical ions; with exception of Ig and Ih the base peaks are mostly populated. Fragmentation pattern characteristic of cleavage of furan derivatives was seen with compounds $Ia - Ie$. The fragmentation pathway C starts with cleavage of a ˙CHO radical, i.e. with elimination of oxygen from the heterocycle and the neighbouring α-carbon and hydrogen. Pathway D commences with splitting of oxygen from the heterocycle with the other α-carbon, bearing the aryl residue, to give the aroyl ion E (Scheme 3). Compound Ih did not undergo the fragmentation charac-
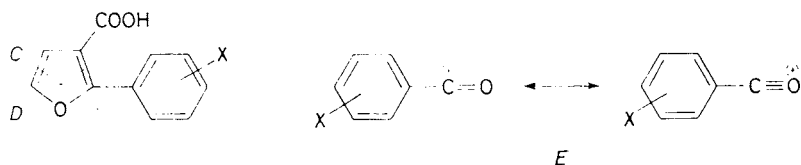
SCHEME 3

teristic of furan derivatives. The most intense peak, associated with cleavage of the ˙COOCH$_3$ radical (m/z 187) was accompanied by the presence of a metastable ion $m^* = 142·15$. The diagnostic fragmentation of furan did not occur even with derivatives If and Ig: compound If had typical fragmentation of nitro derivatives. The molecular radical ion rearranged into a nitrite derivative from which NO˙ radical and a neutral CO molecule were lost (Scheme 4).

The acido-basic properties of acids $Ia - If$ were investigated in 70% dioxane, the molar fraction of which is 0·330, at 25°C, becaue of their low solubility in water.
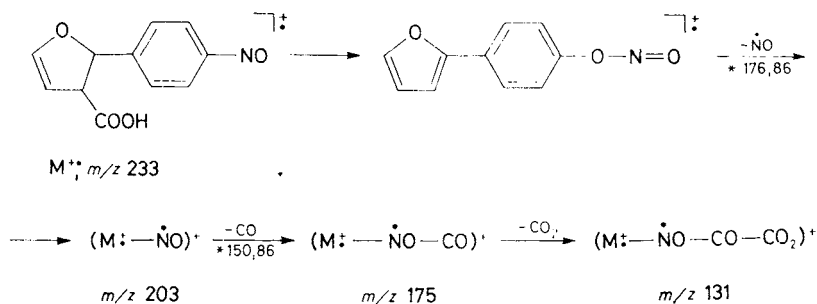
In the first formula for —NO read —NO$_2$.

SCHEME 4

Dissociation constants were determined according to Van Uitert and Hass[11], emploing potentiometric titration with glass indication electrode in accordance with the algorithm described in[12]. Corrections of pH values for the mixture dioxane–water were taken from[13,14]. The activity values were interpolated from data by Harned and Owen[15].

The pK_a values were calculated from equation

$$pK_a = B + \log U_H^0 + \log \left(\gamma^{\pm}\right)^{-1}.$$

where B stands for the measured pH, U_H^0 and γ are constants[15]. The pK_a values thus obtained (Table III) were correlated[16] with σ_p^0 constants determined from reactions having the reaction centre isolated from the conjugated system by the least square method: $pK_a = \left(8.57 \pm 0.02\right) - \left(0.97 \pm 0.04\right)\sigma_p^0$ $\left(r = 0.997, S = 0.04, n = 5\right)$, and σ_p^+ constants, i.e. with constants for conjugated electron-donating substituents: $pK_a = \left(8.40 \pm 0.09\right) - \left(0.59 \pm 0.17\right)\sigma_p^+$ $\left(r = 0.898, S = 0.19, n = 5\right)$. Derivative *Id* was not included into correlation because of its low solubility. As seen, the pK_a values better correlate with σ_p^0 constants, thus evidencing a lowered conjugation between aryl and furan rings due to rotation of the aryl residue out of the molecule plane.

The ionization equilibria of acids *I* were compared with structurally similar (Z)-3--(4-X-phenyl)acrylic acids *II* (Scheme 5). Since the pK_a values of acids *II* were
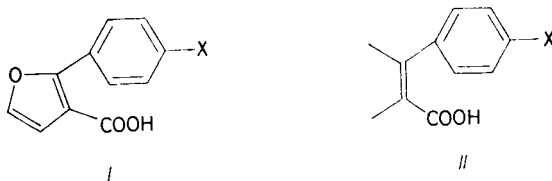
SCHEME 5

TABLE V

Values of slopes ϱ of the relationship $\Delta pK - \varrho\sigma_p^0$

Compound	I_σ^a	I_D^b	Exper.
I	0.88	0.69	0.97
II	0.69	0.69	0.79

[a] Inductive theory of polar effect transmission; [b] electrostatic theory.

measured in a 50% ethanol[17], a conversion factor 0·975 for 70% dioxane, obtained from the pK_a data[17] of 4-substituted benzoic acids measured in 50% ethanol and 70% dioxane, had to be used. The relationship $pK_a = (5·23 \pm 0·02) - (0·79 \pm 0·04)$ σ_p^0 ($r = 0·994$, $S = 0·04$, $n = 6$) was obtained when employing σ_p^0 constants; it indicates a higher acidity of acids I towards II ($\varrho_I/\varrho_{II} = 1·23$).

Considering the acidity of acids I and II in ΔpK_a units (positive values of line slopes ϱ), one can try a test of alternative theories of polar effect transmission[18] (Table V). The inductive theory of polar effect transmission[19] I_p^0 qualitatively well predicts acidity of all compounds ($\varrho_I/\varrho_{II} = 1·28$); on the other hand, the electrostatic theory [18]F_D fails with arylfuran derivatives I. This fact, however, cannot be considered a proof for superiority of inductive theory over the electrostatic one, since an insufficient interaction of the furan ring dipole with the carbonyl group proton was taken into account when applying the latter. Correlation of $\nu(CO)$ vs Hammett's σ_p^0 and σ_p^+ constants revealed following relationships: $\nu(CO) = (1\,691·0 \pm 0·20) - (5·33 \pm 0·60)\,\sigma_p^0$ ($r = 0·977$, $S = 0·48$, $n = 6$), and $\nu(CO) = (1·689·2 \pm 0·4) - (3·38 \pm 0·72)\,\sigma_p^+$ ($r = 0·925$, $S = 0·85$, $n = 6$). Also in this case the σ_p^0 Hammett's constants better fit the correlation, what is in agreement with the suggestion of non--planarity of these systems.

EXPERIMENTAL

Melting points were determined on a Kofler micro hot-stage. The IR spectra of compounds in KBr pellets (1 mg/1 g KBr) were measured with a UR-20 (Zeiss, Jena) spectrophotometer with reading accuracy $\pm 1\,cm^{-1}$. The UV spectra of methanolic solutions ($5 . 10^{-5}\,mol\,l^{-1}$) were taken with a Specord UV-VIS (Zeiss, Jena) apparatus, reading accuracy ± 1 nm. The ^1H and ^{13}C NMR spectra of hexadeuteriodimethyl sulfoxide solutions were recorded with a Tesla BS-487 A (80 MHz) and Jeol FX-100 (25 MHz) instruments, respectively, tetramethyl-silane being the internal reference. Electron impact mass spectra were recorded with an MS 902 S (AEI, Manchester) spectrometer at 70 eV electron energy, 100 μA trap current and ion source temperature 70–180°C corresponding to volatility of the particular sample.

Determination of pK_a Values

The pH values of 20 ml initial volume samples were measured with a digital pH-meter Orion 801 A (0·001 reading accuracy), employing a combined glass electrode Radelkis OP-807-1/A at 25·0 $\pm$ 0·1 C. The atmospheric carbon dioxide was prevented from interference with samples measured by working in an argon atmosphere. The acid was titrated with $5·5 . 10^{-2}$M potassium hydroxide; the total molar ionic strength at the half-neutralisation point was approximately 0·01. For titration the piston burette Metrohm E 275 enabling dosing to a precision of $5 . 10^{-3}$ ml was employed.

The pH-metering equipment was standardized against aqueous solutions of potassium hydrogen phthalate and sodium tetraborate any time before and after titrations. Redistilled water and dioxane purified successively by boiling with potassium hydroxide, sodium metal and distillation were used.

2-(X-Phenyl)-3-furancarboxylic Acids *Ia—Ih*

A) Substituted aniline (0·03 mol) dissolved in 36% hydrochloric acid (9·6 ml, 90 mmol) was cooled to 0°C, diazotized with sodium nitrite (2·1 g, 30 mmol) in water (10 ml) at 0—5°C, and stirred for 10 min. 3-Furancarboxylic acid (2·2 g, 20 mmol) in acetone (5 ml) and copper dichloride dihydrate (1·38 g, 8 mmol) in water (4 ml) were added to the filtered diazotized solution and the mixture was left to stand at room temperature for 48 h. The separated precipitate was filtered off, the filtrate was extracted with ether (3 × 50 ml), the ethereal solution was dried and the organic solvent was distilled off. By extraction virtually the total unreacted 3-furancarboxylic acid (m.p. 104 — 111°C) was recovered. The precipitate dissolved in 5% sodium carbonate was refluxed with charcoal, filtered and acidified with dilute hydrochloric acid (1 : 1) to yield 2-aryl-3--furancarboxylic acid. This product was purified by crystallization.

B) When procedure *A* led to an oily product instead to a precipitate, the former was extracted with chloroform, the solvent was evaporated and the residue was worked up as with method *A*.

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