SOME DERIVATIVES OF 5-ARYL-2-FURANCARBOXYLIC ACIDS

A. KRUTOŠÍKOVÁ and J. KOVÁČ

Department of Organic Chemistry,
Slovak Institute of Technology, 880 37 Bratislava

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The preparation of chlorides, amides, and N-substituted and N,N-disubstituted amides of 5-aryl-2-furancarboxylic acids is described.

TABLE I

Chlorides of 5-Aryl-2-furancarboxylic Acids

Compound	Formula (m.w.)	Calculated/Found % C	% H	% Cl	M.p., °C[a] (yield, %)	λ_{max} (log ε)	ν(C=O)
I	$C_{11}H_6ClNO_4$ (251·4)	52·50 52·40	2·40 2·38	14·08 13·92	144—146 (54)	345 (4·52)	1 762
II	$C_{11}H_6ClNO_4$ (251·4)	52·50 52·38	2·40 2·36	14·08 14·06	117 (40)	322 (4·44)	1 761
III	$C_{11}H_6ClNO_4$ (251·4)	52·50 52·39	2·40 2·38	14·08 14·02	65—66 (60)	317 (4·24)	1 760
IV	$C_{11}H_6Cl_2O_2$ (241·1)	54·80 54·78	2·51 2·50	29·41 29·40	76 (90)	336 (4·84)	1 756
V	$C_{11}H_6Cl_2O_2$ (241·1)	54·80 54·76	2·51 2·46	29·41 29·36	68 (65)	325 (4·44)	1 758
VII	$C_{12}H_9ClO_2$ (220·6)	65·32 65·30	4·11 4·08	16·06 16·00	66—67 (70)	335 (4·44)	1 756
VIII	$C_{12}H_9ClO_3$ (236·6)	60·90 60·86	3·83 3·78	14·98 14·88	95—96 (80)	351 (4·52)	1 754
IX	$C_{11}H_5Cl_3O_2$ (275·5)	47·95 47·72	1·83 1·80	38·60 38·58	115—116 (75)	333 (4·67)	1 757

[a] Compounds *I*—*V*, *VII*, *IX* were crystallised from n-heptane, compound *VIII* from toluene.

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In our previous work[1-3] we synthesized and studied 5-aryl-2-furancarboxylic acids and their methyl esters. As a continuation of this work we prepared now by treatment with thionyl chloride the corresponding acid chlorides (Table I) which were then transformed into amides by reaction with ammonia. In order to study the biological activity of this series of compounds we transformed 5-(nitrophenyl)-2-furoyl chlorides also into N-substituted and N,N-disubstituted amides by treatment with some primary or secondary amines (Table II, III).

EXPERIMENTAL

5-Aryl-2-furoyl Chlorides *I—IX*

A mixture of 5-aryl-2-furancarboxylic acid (0·04 mol) and thionyl chloride (20 ml) was heated to 80°C for 3 hours. The excess thionyl chloride was distilled off and the residue was crystallised.

TABLE II
Amides of 5-Aryl-2-furancarboxylic Acids

Compound	Formula (m.w.)	Calculated/Found % C	% H	% N	M.p., °C[a] (yield, %)	λ_{max} (log ε)	ν(C=O) cm^{-1}
X	$C_{11}H_8N_2O_4$ (232·2)	56·93 / 56·88	3·47 / 3·40	12·06 / 12·20	200—202 (65)	350 (4·43)	1 687
XI	$C_{11}H_8N_2O_4$ (232·2)	56·93 / 56·90	3·47 / 3·40	12·06 / 12·16	205—207 (63)	302 (4·35)	1 685
XII	$C_{11}H_8N_2O_4$ (232·2)	56·93 / 56·86	3·47 / 3·50	12·06 / 11·98	135—136 (64)	290 (4·22)	1 687
XIII	$C_{11}H_8ClNO_2$ (221·6)	59·61 / 59·48	3·63 / 3·59	6·32 / 6·40	191—192 (58)	308 (4·42)	1 685
XIV	$C_{11}H_8ClNO_2$ (221·6)	59·61 / 59·60	3·63 / 3·65	6·32 / 6·36	135—136 (60)	301 (4·34)	1 684
XV	$C_{12}H_8F_3NO_2$ (255·2)	56·48 / 56·38	3·15 / 3·20	5·48 / 5·50	162—164 (55)	302 (4·41)	1 685
XVI	$C_{12}H_{11}NO_2$ (201·2)	70·63 / 70·60	5·50 / 5·48	6·95 / 6·90	171—172 (57)	303 (4·48)	1 681
XVII	$C_{12}H_{11}NO_3$ (217·2)	66·35 / 66·30	5·10 / 5·10	6·44 / 6·40	182—183 (58)	312 (4·44)	1 680
XVIII	$C_{11}H_7Cl_2NO_2$ (256·1)	51·59 / 51·50	2·74 / 2·70	5·40 / 5·38	193—194 (64)	308 (4·45)	1 684

[a] From ethanol.

TABLE III

N-Alkyl and N,N-Dialkyl Amides of 5-Aryl-2-furancarboxylic Acids

Compound	Formula (m.w.)	Calculated/Found % C	% H	% N	M.p., °C[a] (yield)	λ_{max} (log ε)	ν(C=O) cm^{-1}
XIX	$C_{12}H_{10}N_2O_4$ (246·2)	58·54 58·50	4·09 4·00	11·37 11·30	181—182 (56)	351 (4·36)	1 670
XX	$C_{13}H_{12}N_2O_4$ (260·2)	60·00 60·20	4·64 4·62	10·76 10·70	171—172 (58)	352 (4·38)	1 633
XXI	$C_{13}H_{12}N_2O_4$ (260·2)	60·00 60·12	4·64 4·60	10·76 10·72	173—175 (59)	353 (4·28)	1 664
XXII	$C_{14}H_{12}N_2O_4$ (272·3)	61·76 61·70	4·44 4·40	10·29 10·30	156—158 (50)	351 (4·30)	1 670
XXIII	$C_{14}H_{14}N_2O_4$ (274·3)	61·31 61·20	5·14 5·04	10·21 10·11	171—173 (55)	352 (4·41)	1 665
XXIV	$C_{14}H_{14}N_2O_4$ (274·3)	61·31 61·16	5·14 5·20	10·21 10·02	189—190 (52)	354 (4·38)	1 664
XXV	$C_{15}H_{16}N_2O_4$ (288·3)	62·49 62·50	5·53 5·60	9·71 9·80	125—126 (54)	354 (4·37)	1 629
XXVI	$C_{12}H_{10}N_2O_4$ (246·2)	58·54 58·44	4·09 4·02	11·37 11·30	143—144 (55)	304 (4·40)	1 629
XXVII	$C_{13}H_{12}N_2O_4$ (260·2)	60·00 60·10	4·64 4·60	10·76 10·72	145—146 (54)	303 (4·43)	1 562
XXVIII	$C_{13}H_{12}N_2O_4$ (260·2)	60·00 60·02	4·64 4·68	10·76 10·68	168—169 (55)	303 (4·43)	1 667
XXIX	$C_{14}H_{12}N_2O_4$ (272·3)	61·76 61·68	4·44 4·32	10·29 10·09	173—175 (53)	303 (4·37)	1 663
XXX	$C_{14}H_{14}N_2O_4$ (274·3)	61·31 61·21	5·14 5·07	10·21 10·10	173—175 (52)	303 (4·43)	1 660
XXXI	$C_{14}H_{14}N_2O_4$ (274·3)	61·31 61·16	5·14 5·06	10·21 10·11	221—223 (53)	305 (4·43)	1 622
XXXII	$C_{12}H_{10}N_2O_4$ (246·2)	58·54 58·48	4·09 4·00	11·37 11·30	110—111 (52)	288 (4·17)	1 670
XXXIII	$C_{13}H_{12}N_2O_4$ (260·2)	60·00 60·21	4·64 4·60	10·76 10·68	140 (50)	294 (4·17)	1628
XXXIV	$C_{13}H_{12}N_2O_4$ (260·2)	60·00 59·96	4·64 4·60	10·76 10·70	85—87 (50)	286 (4·15)	1 665
XXXV	$C_{14}H_{12}N_2O_4$ (272·3)	61·76 61·66	4·44 4·58	10·29 10·19	60—61 (48)	290 (4·19)	1 669
XXXVI	$C_{14}H_{14}N_2O_4$ (274·3)	61·31 61·21	5·14 5·07	10·21 10·32	94—95 (49)	290 (4·22)	1 662

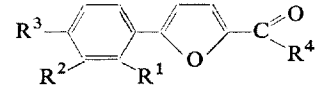
[a] From ethanol.

5-Aryl-2-furancarboxamides *X—XVIII*

Ammonia was introduced at 5°C into a solution of 5-aryl-2-furoyl chloride (0·02 mol) in benzene (50 ml) for 10 min. The mixture was allowed to stand for 1 hour at room temperature, and the separated ammonium chloride was filtered and washed with benzene. The combined benzene solutions were washed successively with 5% hydrochloric acid, water, 5% sodium carbonate solution and again with water till neutral reaction. After drying over anhydrous sodium sulphate the benzene was distilled off and the residue crystallised.

N-Substituted Amides of 5-Aryl-2-furancarboxylic Acids

A solution of an alkyl or dialkyl amine in benzene (10 ml) was added at 5°C to a stirred solution of 5-aryl-2-furoyl chloride (0·02 mol) in benzene (50 ml) and the mixture was set aside overnight. The isolation procedure was analogous to that described in the preceding experiment.



No	R^1	R^2	R^3	R^4	No	R^1	R^2	R^3	R^4
I	H	H	NO_2	Cl	*XIX*	H	H	NO_2	$NHCH_3$
II	H	NO_2	H	Cl	*XX*	H	H	NO_2	$N(CH_3)_2$
III	NO_2	H	H	Cl	*XXI*	H	H	NO_2	$NHCH_2CH_3$
IV	H	H	Cl	Cl	*XXII*	H	H	NO_2	$NHCH_2CH{-}CH_2$
V	Cl	H	H	Cl	*XXIII*	H	H	NO_2	$NHCH_2CH_2CH_3$
VI	H	CF_3	H	Cl	*XXIV*	H	H	NO_2	$NHCH(CH_3)_2$
VII	H	H	CH_3	Cl	*XXV*	H	H	NO_2	$N(CH_2{-}CH_3)_2$
VIII	H	H	CH_3O	Cl	*XXVI*	H	NO_2	H	$NH{-}CH_3$
IX	H	Cl	Cl	Cl	*XXVII*	H	NO_2	H	$N(CH_3)_2$
X	H	H	NO_2	NH_2	*XXVIII*	H	NO_2	H	$NHCH_2CH_3$
XI	H	NO_2	H	NH_2	*XXIX*	H	NO_2	H	$NHCH_2CH{=}CH_2$
XII	NO_2	H	H	NH_2	*XXX*	H	NO_2	H	$NHCH_2CH_2CH_3$
XIII	H	H	Cl	NH_2	*XXXI*	H	NO_2	H	$NHCH(CH_3)_2$
XIV	Cl	H	H	NH_2	*XXXII*	NO_2	H	H	$NHCH_3$
XV	H	CF_3	H	NH_2	*XXXIII*	NO_2	H	H	$N(CH_3)_2$
XVI	H	H	CH_3	NH_2	*XXXIV*	NO_2	H	H	$NHCH_2CH_3$
XVII	H	H	CH_3O	NH_2	*XXXV*	NO_2	H	H	$NHCH_2CH{=}CH_2$
XVIII	H	Cl	Cl	NH_2	*XXXVI*	NO_2	H	H	$NHCH(CH_3)_2$

Spectral Measurements

The infrared absorption spectra of the synthesized compounds were measured in the region 3600—800 cm^{-1} on a double-beam UR-20 spectrophotometer, calibrated with a 20 μm polystyrene foil. The IR spectra of 5-aryl-2-furoyl chlorides were taken in 1 . 10^{-2}M tetrachloromethane solutions, other compounds were measured in chloroform, concentration 2 . 10^{-2}M, in 0·4 mm NaCl cells.

Electronic absorption spectra of the compounds *I*—*XXXVI* were taken on a Specord UV VIS (Zeiss, Jena) instrument in the region 200—480 nm. The measurements were performed in dioxane at room temperature in 1 cm cells, concentration 4 . 10^{-5}M.

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