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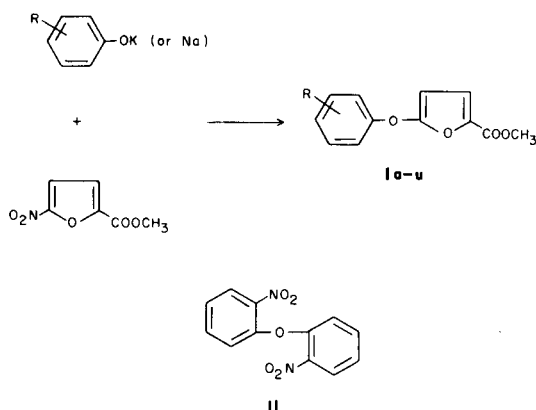
Twenty one methyl 5-phenoxy-2-furancarboxylates prepared from the reaction of methyl 5-nitro-2-furancarboxylate with phenoxides *via* displacement of the nitro group. In the reaction of potassium 2-nitrophenoxide with methyl 5-nitro-2-furancarboxylate at 110°-120°, 2,2'-dinitrodiphenyl ether was obtained as a main product.

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Recently, it was found that the nucleophilic substitution of 5-nitro-2-furancarbaldehyde by phenoxide ions easily gave 5-phenoxy-2-furancarbaldehydes (2).

In the continuous work, we now provide the first examples of the preparation of methyl 5-phenoxy-2-furancarboxylates (3) by the replacement of the nitro group with a phenoxy group on methyl 5-nitro-2-furancarboxylate. There are no reports on such a nucleophilic displacement processes involving 5-nitro-2-furancarboxylates (4,5).

Scheme



When a mixture of methyl 5-nitro-2-furancarboxylate, phenoxides, and dimethyl sulfoxide was heated at 80-90° for 10 hours, methyl 5-phenoxy-2-furancarboxylates (Ia-u) were formed in good yields. The structures of Ia-u were assigned by their elemental analysis and spectral data as shown in Table I and II. In the reaction with potassium 2-nitrophenoxide, 2,2'-dinitrodiphenyl ether (II) was obtained as a by-product. Also, when the reaction temperature was elevated at 110-120°, mainly II was produced. The structure of II was assigned with the specimen prepared from the reaction of potassium 2-nitrophenoxide with 2-chloronitrobenzene by Randall's method (6).

However, the mechanism of the formation of II in this reaction is at present unknown.

Thus, it was established that the reaction of methyl 5-nitro-2-furancarboxylate with phenoxides gives methyl 5-phenoxy-2-furancarboxylates in which the substituent on the benzene ring can be varied by the electronic character from nitro to methoxyl group. These results are similar to a series of the reaction with 5-nitro-2-furancarbaldehyde (2). It is proposed that compounds Ia-u may be utilized as important starting materials from which derive further derivatives.

EXPERIMENTAL

All melting points and boiling points are uncorrected. Infrared spectra were recorded using a Jasco IRA-1 spectrophotometer. Nuclear magnetic resonance spectra were recorded on JEOL JNM-60HL and PS-100 spectrophotometers with tetramethylsilane as an internal standard. Mass spectra were obtained (direct inlet) on a Shimadzu LKB-900 instrument. Sodium hydride (50%) was purchased from Wako Chemical Industry, LTD.

Methyl 5-Phenoxy-2-furancarboxylates (Ia-u).

A.

A mixture of potassium phenoxides (0.07 mole), 10 g (0.058 mole) of methyl 5-nitro-2-furancarboxylate, and 100 ml of dimethyl sulfoxide was heated at 80-90° for 10 hours under stirring. After cooling, the mixture was poured into ice-water. The produced precipitate was filtered and recrystallized from suitable solvents to give Ia-c,i, respectively.

B.

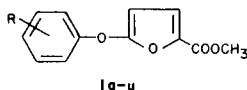
A mixture of potassium phenoxides (0.07 mole), 10 g (0.058 mole) of methyl 5-nitro-2-furancarboxylate, and 100 ml of dimethyl sulfoxide was heated at 80-90° for 10 hours under stirring. After cooling, the mixture was poured into ice-water. The oil produced was extracted with benzene. The benzene extract was washed with 5% potassium hydroxide solution and water, dried over calcium chloride, and evaporated. The residual oil was distilled under vacuum to give Ig,j,o,r,s,u, respectively.

C.

To a solution of phenols (0.07 mole) in 100 ml of dimethyl sulfoxide was added 3.4 g. (0.14 mole) of 50% sodium hydride under vigorous stirring. To the above mixture was added 10 g. (0.058 mole) of methyl

Table I

Methyl 5-Phenoxy-2-furancarboxylates



Compound No.	R	Yield (%)	Bp (°C)/torr or Mp (°C)	Recrystallization	Formula	Analysis		
						C	H	Calcd. (Found) N
Ia	2-NO ₂	33	100-102	MeOH	C ₁₂ H ₉ NO ₆	54.76 (54.63)	3.54 3.61	5.32 5.21
Ib	3-NO ₂	78	118-119	MeOH	C ₁₂ H ₉ NO ₆	54.76 (54.76)	3.54 3.69	5.32 5.36
Ic	4-NO ₂	42	144-146	MeOH	C ₁₂ H ₉ NO ₆	54.76 (54.80)	3.54 3.59	5.32 5.06
Id	2-COOCH ₃	52	185/2	---	C ₁₄ H ₁₂ O ₆	60.87 (60.70)	4.38 4.32	
Ie	3-COOCH ₃	65	79-81	Petroleum benzin	C ₁₄ H ₁₂ O ₆	60.87 (61.04)	4.38 4.53	
If	4-COOCH ₃	84	92-94	Petroleum benzin	C ₁₄ H ₁₂ O ₆	60.87 (60.69)	4.38 4.57	
Ig	2-Cl	74	177-178/6.5	---	C ₁₂ H ₉ ClO ₆	57.05 (57.19)	3.59 3.67	
Ih	3-Cl	74	55-57	Petroleum benzin	C ₁₂ H ₉ ClO ₆	57.05 (57.00)	3.59 3.61	
Ii	4-Cl	78	68-69	Petroleum benzin	C ₁₂ H ₉ ClO ₆	57.05 (57.08)	3.59 3.73	
Ij	H	75	150-151/4	---	C ₁₂ H ₁₀ O ₄	66.05 (66.21)	4.62 4.79	
Ik	3-NHCOCH ₃	50	94-96	Benzene	C ₁₄ H ₁₃ NO ₅	61.09 (61.00)	4.76 4.70	4.90 5.23
Il	4-NHCOCH ₃	81	133-135	Benzene	C ₁₄ H ₁₃ NO ₅	61.06 (61.06)	4.81 4.81	4.84
Im	2-C ₂ H ₅	80	163-165/5	---	C ₁₄ H ₁₄ O ₄	68.28 (68.15)	5.73 5.53	
In	3-C ₂ H ₅	59	160/3	---	C ₁₄ H ₁₄ O ₄	68.28 (68.47)	5.73 5.93	
Io	4-C ₂ H ₅	69	159-161/3	---	C ₁₄ H ₁₄ O ₄	68.28 (68.20)	5.73 5.81	
Ip	2-CH ₃	85	147-148/3.5	---	C ₁₃ H ₁₂ O ₄	72.21 (72.11)	5.59 5.56	
Iq	3-CH ₃	70	156-157/4	---	C ₁₃ H ₁₂ O ₄	72.34 (72.05)	5.47 5.44	
Ir	4-CH ₃	74	156/3.5	---	C ₁₃ H ₁₂ O ₄	72.21 (72.05)	5.59 5.44	
Is	2-OCH ₃	81	173-174/4	---	C ₁₃ H ₁₂ O ₅	62.90 (62.61)	4.87 5.06	
It	3-OCH ₃	57	173/3.5	---	C ₁₃ H ₁₂ O ₅	62.90 (63.02)	4.87 5.12	
Iu	4-OCH ₃	53	175-177/3	---	C ₁₃ H ₁₂ O ₅	62.90 (62.67)	4.87 5.09	

solution and water, dried over calcium chloride, and evaporated down. The residual oil was distilled two times under vacuum to give Id,m,n,p,q,t, respectively.

D.

To a solution of phenols (0.07 mole) in 100 ml of dimethyl sulfoxide was added 3.4 g (0.14 mole) of 50% sodium hydride under vigorous stirring. To an above mixture was added 10 g (0.058 mole) of methyl 5-nitro-2-furancarboxylate, and heated at 80-90° for 10 hours under stirring, then poured into ice-water. The produced oil was extracted with benzene. The benzene extract was washed with 5% potassium hydroxide solution and water, dried over calcium chloride, and evaporated down. The residual oil was distilled two times under vacuum to give Id,m,n,p,q,t, respectively.

2,2'-Dinitrodiphenyl Ether (II).

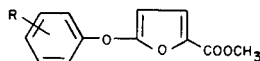
A mixture of 12.4 g (0.07 mole) of potassium 2-nitrophenoxide, 10 g (0.058 mole) of methyl 5-nitro-2-furancarboxylate, and 100 ml of dimethyl sulfoxide was heated at 110-120° for 5 hours. After cooling, the mixture was poured into ice-water and extracted with benzene. The benzene extract was washed with 5% potassium hydroxide solution and water, dried over calcium chloride, and evaporated down. The residue was recrystallized from methanol to give 5.3 g of II as yellow prisms, mp 120-122°; ir (nujol): ν max 1340, 1515 cm⁻¹ (NO₂); ms:m/e 260 (M⁺); nmr (deuterioacetone): δ 7.10-8.25 (m).

Anal. Calcd. for C₁₂H₈N₂O₅: C, 55.39; H, 3.10; N, 10.77. Found: C, 55.67; H, 3.10; N, 10.77.

This compound was identified by a mixed melting point test and various spectral comparison with II prepared by Randall's method (6).

Table II

Methyl 5-Phenoxy-2-furancarboxylates



Compound No.	MS m/e (M ⁺)	IR ν Max (nujol) Cm^{-1} for C=O	¹ O-u	NMR (a) δ (deuteriochloroform)
Ia	--(b)	1720		3.76 (3H, s, CH ₃), 5.89 (1H, d, J = 3.8 Hz, F-4H), 7.27 (1H, d, J = 3.8 Hz, F-3H), 7.40-8.20 (4H, m, phenyl H)
Ib	263	1720		3.84 (3H, s, CH ₃), 5.78 (1H, d, J = 3.8 Hz, F-4H), 7.19 (1H, d, J = 3.8 Hz, F-3H), 7.10-8.10 (4H, m phenyl H)
Ic	263	1720		3.88 (3H, s, CH ₃), 5.87 (1H, d, J = 3.8 Hz, F-4H), 7.21 (1H, d, J = 3.8 Hz, F-3H), 7.19 (2H, d, J = 9 Hz, phenyl H), 8.23 (2H, d, J = 9 Hz, phenyl H)
Id	276	1720 (broad)		3.83 (6H, s, CH ₃ x 2), 5.42 (1H, d, J = 3.8 Hz, F-4H), 7.13 (1H, d, J = 3.8 Hz, F-3H), 7.00-8.05 (4H, m, phenyl H)
Ie	276	1720 (broad)		3.87 (3H, s, CH ₃), 3.92 (3H, s, CH ₃), 5.62 (1H, d, J = 3.8 Hz, F-4H), 7.15 (1H, d, J = 3.8 Hz, F-3H), 7.10-8.00 (4H, m, phenyl H)
If	276	1730		3.87 (3H, s, CH ₃), 3.91 (3H, s, CH ₃), 5.72 (1H, d, J = 3.8 Hz, F-4H), 7.17 (1H, d, J = 3.8 Hz, F-3H), 7.10 (2H, d, J = 9 Hz, phenyl H), 8.03 (2H, d, J = 9 Hz, phenyl H)
Ig	252	1720		3.87 (3H, s, CH ₃), 5.49 (1H, d, J = 3.8 Hz, F-4H), 6.90-7.65 (5H, m, F-3H and phenyl H)
Ih	252	1720		3.87 (3H, s, CH ₃), 5.63 (1H, d, J = 3.8 Hz, F-4H), 6.80-7.50 (5H, m, F-3H and phenyl H)
Ii	252	1710		3.80 (3H, s, CH ₃), 5.47 (1H, d, J = 3.8 Hz, F-4H), 7.00 (1H, d, J = 3.8 Hz, F-3H), 6.94 (2H, d, J = 9 Hz, phenyl H)
Ij	218	1730		3.83 (3H, s, CH ₃), 5.51 (1H, d, J = 3.8 Hz, F-4H), 6.90-7.52 (5H, m, F-3H and phenyl H)
Ik	275	1665, 1720		2.12 (3H, s, CH ₃), 3.85 (3H, s, CH ₃), 5.57 (1H, d, J = 3.8 Hz, F-4H), 6.70-7.50 (5H, m, F-3H and phenyl H), 8.13 (1H, broad s, NH)
Il	275	1670, 1720		2.09 (3H, s, CH ₃), 3.82 (3H, s, CH ₃), 5.46 (1H, d, J = 3.8 Hz, F-4H), 7.12 (1H, d, J = 3.8 Hz, F-3H), 7.05 (2H, d, J = 9 Hz, phenyl H), 7.50 (2H, d, J = Hz, phenyl H), 8.20 (1H, broad s, NH)
Im	216	1730		1.20 (3H, t, J = 7.5 Hz, CH ₃), 2.69 (2H, q, J = 7.5 Hz, CH ₂), 3.83 (3H, s, CH ₃), 5.33 (1H, d, J = 3.8 Hz, F-4H), 6.80-7.50 (5H, m, F-3H and phenyl H)
In	246	1730		1.21 (3H, t, J = 7.5 Hz, CH ₃), 2.63 (2H, q, J = 7.5 Hz, CH ₂), 3.82 (3H, s, CH ₃), 5.50 (1H, d, J = 3.8 Hz, F-4H), 7.13 (1H, d, J = 3.8 Hz, F-3H), 6.80-7.50 (4H, m, phenyl H)
Io	246	1730		1.35 (3H, t, J = 7.5 Hz, CH ₃), 2.65 (2H, q, J = 7.5 Hz, CH ₂), 3.85 (3H, s, CH ₃), 5.47 (1H, d, J = 3.8 Hz, F-4H), 6.90-7.40 (5H, m, F-3H and phenyl H)
Ip	232	1725		2.27 (3H, s, CH ₃), 3.83 (3H, s, CH ₃), 5.32 (1H, d, J = 3.8 Hz, F-4H), 6.90-7.50 (5H, m, F-3H and phenyl H)
Iq	232	1730		2.34 (3H, s, CH ₃), 3.84 (3H, s, CH ₃), 5.58 (1H, d, J = 3.8 Hz, F-4H), 7.12 (1H, d, J = 3.8 Hz, F-3H), 6.80-7.50 (4H, m, phenyl H)
Ir	232	1730		2.30 (3H, s, CH ₃), 3.83 (3H, s, CH ₃), 5.45 (1H, d, J = 3.8 Hz, F-4H), 6.80-7.35 (5H, m, F-3H and phenyl H)
Is	248	1720		3.78 (6H, s, CH ₃ x 2), 5.30 (1H, d, J = 3.8 Hz, F-4H), 7.10 (1H, d, J = 3.8 Hz, F-3H), 6.70-7.40 (4H, m, phenyl H)
It	248	1720		3.73 (3H, s, CH ₃), 3.80 (3H, s, CH ₃), 5.57 (1H, d, J = 3.8 Hz, F-4H), 7.10 (1H, d, J = 3.8 Hz, F-3H), 6.50-6.80 and 7.10-7.43 (4H, m, phenyl H)
Iu	248	1730		3.72 (3H, s, CH ₃), 3.82 (3H, s, CH ₃), 5.37 (1H, d, J = 3.8 Hz, F-4H), 7.09 (1H, d, J = 3.8 Hz, F-3H), 6.70-7.20 (4H, m, phenyl H)

(a) s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, F: furan ring. (b) Molecular ion peak was not observed.

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