5-NITRO-2-FURYLVINYLATION OF AROMATIC COMPOUNDS

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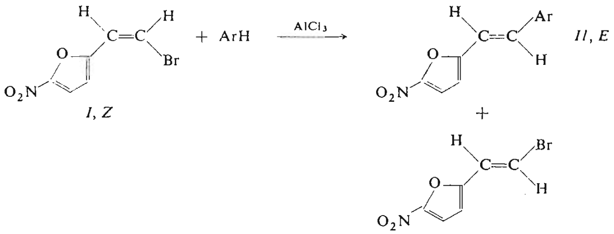
A new synthesis of (*E*)-2-(4-X-phenyl)-1-(5-nitro-2-furyl)ethylenes (X = H, CH_3, OH, OCH_3), 2-(2-naphthyl)-1-(5-nitro-2-furyl)ethylene and 2-(2-thienyl)-1-(5-nitro-2-furyl)ethylene from (*Z*)-2-bromo-1-(5-nitro-2-furyl)ethylene and the respective aromatic or heteroaromatic derivative under catalysis of aluminium chloride is described.

Although 5-nitro-2-furylethylene derivatives of various types are well known, little attention has been paid to the high biological activity of 5-nitro-2-furylvinylenebenzene compounds[1]. They were originally prepared by condensation of 5-nitro-2-furaldehyde with phenylacetic acids followed by a decarboxylation of the product[2], or alternatively, by the Wittig reaction of 5-nitro-2-furaldehyde with suitable benzyl type of ylides[3-5].

We prepared (*E*)-2-(4-X-phenyl)-1-(5-nitro-2-furyl)ethylenes (X = H, CH_3, OH, OCH_3), 2-(2-naphthyl)-1-(5-nitro-2-furyl)-ethylene and 2-(2-thienyl)-1-(5-nitro-2-furyl)ethylene by reacting (Z)-2-bromo-1-(5-nitro-2-furyl)ethylene (*I*) with aromatic or heteroaromatic compounds under catalysis of aluminium chloride (Scheme 1). Compound *I* was prepared by a debrominative decarboxylation of *erythro*-2,3-dibromo-3-(5-nitro-2-furyl)propionic acid[6]. The best isolation technique found was the chromatography on alumina using benzene as eluent. The substitution with benzene derivatives under study took always place in *para*-position[7,8] and with naphthalene or thiophene in position 2. Table I summarizes the products obtained by vinylation of aromates. In addition to compound *II*, (*E*)-2-bromo-1-(5-nitro-2-furyl)ethylene was isolated, the structure of which was corroborated by comparison of both chemical shift and coupling constant data of the ^{1}H-NMR spectrum[6].

The structure of the synthesized compounds follows from the method of preparation, mass and ^{1}H-NMR spectral data. Parent peaks of the mass spectrum of compounds *IIa*, *IIb*, *IId*–*IIf* are represented by molecular ions; the molecular ion of compound *IIc* is also very intense. The fragmentation pattern of molecular ions is exemplified with derivative *IIa*: the species at *m*/*e* 141 originated from fission of the radical $(ON—CO_2)^\cdot$ from the molecular ion, from splitting CO_2 from the fragment ion M – NO (*m*/*e* 185) and from cleavage of CO from the fragment ion M – NO_2

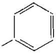
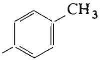
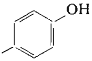
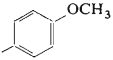
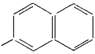
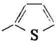
(*m*/*e* 169). Peaks of fragment ions together with their relative abundances are given in the experimental section.



SCHEME 1

TABLE I

5-Nitro-2-furylvinylation of Aromates

Com-pound	Ar	Formula (mol.wt.)	Calculated/Found % C	% H	% N	M.p., °C yield
IIa		$C_{12}H_9NO_3$ (215·2)	66·97 66·85	4·21 4·15	6·50 6·29	110—111 42
IIb		$C_{13}H_{11}NO_3$ (229·2)	68·11 67·92	4·83 4·80	6·11 5·88	120—121 45·5
IIc		$C_{12}H_9NO_4$ (231·2)	62·34 62·21	3·92 3·85	6·05 5·86	208—210 57·6
IId		$C_{13}H_{11}NO_4$ (245·2)	63·67 63·55	4·52 4·47	5·71 5·98	144—145 58·2
IIe		$C_{16}H_{11}NO_3$ (265·3)	72·44 72·22	4·18 4·12	5·28 5·12	102·5—104 74·3
IIf		$C_{10}H_7NO_3S$ (221·2)	54·28 54·11	3·19 3·13	6·33 6·16	117·5—119 67·6

Chemical shift and coupling constant data are listed in Table II. The position of the substituent attached to benzene, naphthalene or thiophene rings was determined on the basis of chemical shifts and multiplicities of the respective protons; thus, the 5-nitro-2-furylvinylene group was found to be attached to *para*-position

TABLE II

^{1}H-NMR Spectra of Derivatives *II* ($CDCl_3$, Tetramethylsilane)

Derivative X	δ, ppm							δ_X, ppm
	H_3	H_4	$H_{2',6'}$	$H_{3',5'}$	H_A	H_B		
IIa	6·53	7·35	7·25—7·52		7·42	6·87		
H	(d)	(d)	(m)		(d)	(d)		
	$J_{3,4}$ = 4 Hz				$J_{A,B}$ = 16·5 Hz			
IIb	6·48	7·33	7·18	7·41	7·36	6·80		2·42
CH_3	(d)	(d)	(d)	(d)	(d)	(d)		(s)
	$J_{3,4}$ = 3·9 Hz		$J_{2',3'}$ = 9·1 Hz		$J_{A,B}$ = 16·5 Hz			
IIc	6·71	7·51	6·85	7·79	7·34	6·90		8·92
OH	(d)	(d)	(d)	(d)	(d)	(d)		(s)
	$J_{3,4}$ = 3·9 Hz		$J_{2',3'}$ = 8·9 Hz		$J_{A,B}$ = 16 Hz			
IId	6·47	7·34	6·90	7·38	7·34	6·72		3·82
OCH_3	(d)	(d)	(d)	(d)	(d)	(d)		(s)
	$J_{3,4}$ = 3·9 Hz		$J_{2',3'}$ = 9 Hz		$J_{A,B}$ = 16·5 Hz			
	H_3	H_4	$H_{1'}$	$H_{3'}$	$H_{4'}$	$H_{5',8'}$	H_A	H_B
IIe	6·55	7·36	8·26	7·73	7·75	7·47—8·21	7·48	6·93
—	(d)	(d)	(d)	(d, d)	(d)	(m)	(d)	(d)
	$J_{3,4}$ = 3·9 Hz		$J_{3',4'}$ = 9·3 Hz		$J_{1',3'}$ = 1·5 Hz		$J_{A,B}$ = 16·1 Hz	
	H_3	H_4	$H_{3'}$	$H_{4'}$	$H_{5'}$	H_A	H_B	
IIf	6·48	7·33	7·20	7·03	7·33	7·50	6·65	
	(d)	(d)	(d)	(d, d)	(d)	(d)	(d)	
	$J_{3,4}$ = 3·9 Hz		$J_{3',4'}$ = 3·8 Hz	$J_{4',5'}$ = 5 Hz	$J_{3',5'}$ = 1·2 Hz	$J_{A,B}$ = 16·3 Hz		

of the benzene ring and to position 2 of the naphthalene or thiophene rings. The coupling constant data associated with protons of the ethylene bond evidence all derivatives to be in the thermodynamically more stable *E* configuration.

EXPERIMENTAL

Melting points were determined on a Kofler block, the ^{1}H-NMR spectra were measured with a Tesla BS 487-C apparatus operating at 80 MHz, mass spectra with an AEI MS 902-S instrument at 70 eV and 100 μA trap current, the UV spectra with a Specord UV VIS spectrophotometer and the IR spectra with a UR 20 Zeiss, Jena apparatus.

2-(4-X-Phenyl)-1-(5-nitro-2-furyl)ethylenes, 2-(2-Naphthyl)-1-(5-nitro-2-furyl)ethylene and 2-(2-Thienyl)-1-(5-nitro-2-furyl)ethylene

The solution of the respective aromate (50 mmol) in 1,2-dichloroethane (10 ml) was added under stirring to a mixture of 2-bromo-1-(5-nitro-2-furyl)ethylene (*I*, 2·18 g, 10 mmol) and aluminium chloride (2 g, 15 mmol) in 1,2-dichloroethane at 0°C. The mixture was after addition stirred at room temperature for 30 min and poured onto ice (20 g) acidified with conc. HCl (20 ml). The organic layer was separated, washed with water, 5% potassium carbonate and dried with $CaCl_2$. The solvent was removed under diminished pressure and the residue chromatographed on alumina, benzene being the eluent. Following substances were prepared from various aromates:

2-*Phenyl*-1-(5-*nitro*-2-*furyl*)*ethylene*. (IIa), from benzene. The UV spectrum (λ_{max}, nm, (log ε), methanol): 221 (4·11), 243 (4·00), 286 (4·23), 406 (4·38). IR spectrum ($\tilde{\nu}$, cm^{-1}, chloroform): 960, 1020, 1295, 1355, 1390, 1475, 1515, 1565, 1606, 1633. Mass spectrum (*m*/*e*): 215 (M^+, 100%), 185 (9), 169 (15), 157 (10), 141 (77), 139 (27), 129 (23), 115 (82), 103 (10), 91 (9), 77 (14), 63 (18), 51 (18), 39 (13).

2-(4-*Methylphenyl*)-1-(5-*nitro*-2-*furyl*)*ethylene* (IIb), from toluene. UV spectrum (λ_{max}, nm, (log ε), methanol): 220 (4·03), 243 (3·89), 280 (4·08), 395 (4·23). IR spectrum ($\tilde{\nu}$, cm^{-1}, chloroform): 950, 1020, 1295, 1355, 1390, 1475, 1510, 1565, 1610, 1634. Mass spectrum (*m*/*e*): 229 (M^+, 100%), 199 (6), 183 (11), 182 (8), 171 (9), 168 (14), 165 (6), 155 (47), 153 (30), 149 (8), 143 (11), 139 (14), 128 (32, 115 (22), 91 (7), 77 (11), 63 (11), 51 (10), 39 (9).

2-(4-*Hydroxyphenyl*)-1-(5-*nitro*-2-*furyl*)*ethylene* (IIc), from phenol. UV spectrum (λ_{max}, nm, (log ε), methanol): 222 (4·03), 244 (3·91), 296 (4·14), 423 (4·31). IR spectrum ($\tilde{\nu}$, cm^{-1}, chloroform): 960, 1020, 1275, 1355, 1390, 1475, 1520, 1570, 1607, 1632. Mass spectrum (*m*/*e*): 231 (M^+, 86%), 201 (11), 185 (5), 184 (5), 173 (19), 157 (100), 145 (12), 139 (12), 131 (22), 128 (57), 115 (11), 102 (14), 91 (14), 77 (24), 65 (14), 63 (20), 51 (22), 39 (19).

2-(4-*Methoxyphenyl*)-1-(5-*nitro*-2-*furyl*)*ethylene* (IId), from anisole. UV spectrum (λ_{max}, nm, (log ε), methanol): 222 (4·15), 244 (4·08), 296 (4·29), 418 (4·47). IR spectrum ($\tilde{\nu}$, cm^{-1}, chloroform): 965, 1035, 1275, 1355, 1380, 1475, 1515, 1577, 1607, 1632. Mass spectrum (*m*/*e*): 245 (M^+, 100%), 215 (10), 199 (15), 187 (15), 184 (25), 171 (51), 167 (14), 156 (20), 145 (11), 141 (17), 139 (17), 128 (70), 115 (20), 102 (19), 89 (13), 77 (14), 63 (17), 51 (14), 39 (11).

2-(2-*Naphthyl*)-1-(5-*nitro*-2-*furyl*)*ethylene* (IIe), from naphthalene. UV spectrum (λ_{max}, nm, (log ε), methanol): 227 (4·52), 258 (4·14), 318 (4·03), 411 (4·34). IR spectrum ($\tilde{\nu}$, cm^{-1}, chloroform) 960, 1025, 1285, 1355, 1390, 1485, 1520, 1530, 1570, 1632. Mass spectrum (*m*/*e*): 265 (M^+, 100%), 219 (31), 218 (28), 201 (16), 191 (81), 190 (55), 189 (81), 165 (28), 152 (23), 139 (5), 115 (6), 95 (9), 76 (9), 63 (9), 51 (5), 39 (5).

2-(2-*Thienyl*)-1-(5-*nitro*-2-*furyl*)*ethylene* (IIf), from thiophene. UV spectrum (λ_{max}, nm, (log ε), methanol): 221 (4·06), 297 (4·07), 414 (4·36), IR spectrum ($\tilde{\nu}$, cm^{-1}, chloroform): 950, 1 025, 1 280, 1 355, 1 390, 1 475, 1 515, 1 535, 1 575, 1 627. Mass spectrum (*m*/*e*): 221 (M$^+$, 100%), 191 (6), 175 (12), 163 (14), 147 (90), 135 (9), 121 (18), 115 (6), 103 (17), 97 (7), 91 (8), 89 (5), 77 (17), 69 (18), 63 (20), 51 (13), 39 (16).

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