NEW SYNTHESIS OF 2-(4-NITROPHENYL)-1-(5-NITRO-2-FURYL)ETHYLENE AND 2-(4-ETHOXYCARBONYLPHENYL)-1-(5-NITRO-2-FURYL)ETHYLENE

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(*E*)-2-Ar-1-(5-nitro-2-furyl)ethylenes (where Ar is $O_2N—C_6H_4—$ or $H_5C_2OOC—C_6H_4—$) were prepared by reaction of aryldiazonium salts with 3-(5-nitro-2-furyl)-2-propenoic acid or 2-bromo-1-(5-nitro-2-furyl)ethylene. Photochemical modification of the Meerwein reaction was also checked.

Biologically most active 5-nitro-2-furan derivatives are found among benzene derivatives with an attached 5-nitro-2-furylvinyl group, particularly benzoic acid derivatives[1,2]. In our previous papers[3-5] we described a new synthesis of 2-aryl-1-(5-nitro-2-furyl)ethylenes consisting in the reaction of (Z)-2-bromo-1-(5-nitro-2-furyl)ethylene with aromatic or heteroaromatic compounds under conditions of Friedel–Crafts reaction. Our recent aim has been to prepare the corresponding ethylenes containing also electron accepting substituents attached to the aromatic nucleus. The literature[6] reports reactions of diazonium salts with various olefinic substrates in the presence of a catalyst. Thus, 4-nitrobenzenediazonium chloride reacts wih 3-(2-furyl)-2-propenoic acid to give 2-(4-nitrophenyl)-1-(2-furyl)ethylene as the principal product (23%), along with 2-(4-nitrophenyl)-1-(5-(4-nitrophenyl)-2-furyl)ethylene, 3-(5-(4-nitrophenyl)-2-furyl)-2-propenoic acid and 4-nitro-1-chlorobenzene[7-9]. Also a modification of the Meerwein reaction is known[10] which makes use of the photoreduction of chlorocupric complexes (Cu(II) to Cu(I)) (ref.[11]). The olefin acts as the reducing agent since no Cu(I) salt is formed in its absence.

We have now studied the potential preparation of 2-aryl-1-(5-nitro-2-furyl)ethylenes by the reaction of 3-(5-nitro-2-furyl)-2-propenoic acid or 2-bromo-1-(5-nitro-2-furyl)ethylene with aryldiazonium salts. containing electron accepting substituents. Although the reaction took place, yields of the desired products were low (~14%). If the reaction was carried out in the absence of base (Na_2CO_3), the yields were even lower (4 – 6%). The best yields were obtained with a solid diazonium salt. The classical reaction conditions in the reaction with 4-nitrobenzenediazonium chloride or tetrafluoroborate afforded, in addition to the principal product, also the product of substitution of the nitro group on the furan nucleus, *i.e.* (2-(4-nitrophenyl)-1-(5-(4-nitrophenyl)-2-furyl)ethylene, a product of Sandmayer reaction and the starting olefin.

We tried also the photochemical modification of the Meerwein reaction but the yields were also poor. This modification did not afford any product of substitution of the nitro group on the furan nucleus which indicates other reaction course than that of the classical Meerwein reaction, as already described by Becker and Israel[10].

The structure of the prepared compounds follows from their ^1H NMR spectra. Chemical shifts and coupling constants are given in Table I. Chemical shifts of the ethylenes, where the substituent on the aromatic nucleus R = H, CH_3 or OCH_3, are identical with those published in ref.[3] and therefore they are not listed in our paper. The coupling constants of ethylenes, where R = NO_2 or $COOC_2H_5$, are solvent-dependent. In deuteriochloroform both these compounds exhibit a doublet ($J_{A,B}$ = 16·5–16·6 Hz), confirming the thermodynamically more stable (*E*)-configuration. In hexadeuterioacetone, the ethylenic protons of the compound R = NO_2 show a singlet and for R = $COOC_2H_5$ almost a singlet (the distance of the ethylenic signals is 3·1 Hz).

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. ^1H NMR spectra were measured on a Tesla NMR BS 487 C (80 MHz) instrument. Mass spectra were taken on an MS 902 S spectrometer (70 eV, 100 μA).

TABLE I

^1H NMR spectral data for 2-(4-R-phenyl)-1-(5-nitro-2-furyl)ethylenes (δ, ppm; tetramethylsilane)

R	Solvent	H_3d H_4d ($J_{3,4}$ Hz)	H_Ad H_Bd ($J_{A,B}$ Hz)	$H_{2',6'}$d $H_{3',6'}$d ($J_{2',3'}$ Hz)
NO_2	C^2HCl_3	6·68 7·38 (4·0)	7·45 7·02 (16·5)	7·66 8·25 (8·9)
$COOC_2H_5$[a]	C^2HCl_3	6·59 7·36 (3·9)	7·47 6·95 (16·6)	7·57 8·06 (8·5)
NO_2	$C^2H_3COC^2H_3$	6·97 7·55 (4·0)	7·46 (s)	7·92 8·25 (9·0)
$COOC_2H_5$[b]	$C^2H_3COC^2H_3$	6·95 7·57 (4·0)	7·42 (s)	7·80 8·05 (8·6)

[a] δ_{CH_2} = 4·38 (q), δ_{CH_3} = 1·36 (t); [b] δ_{CH_2} = 4·37 (q), δ_{CH_3} = 1·37 (t).

Reaction of 4-Nitrobenzenediazonium Chloride with 3-(5-Nitro-2-furyl)-2-propenoic Acid

A mixture of 4-nitroaniline (6·9 g; 0·05 mol), conc. hydrochloric acid (30 ml) and water (15 ml) was diazotized with sodium nitrite (3·65 g) in water (20 ml) at 0—5°C. A solution of 3-(5-nitro-2-furyl)-2-propenoic acid (9·2 g; 0·05 mol) in acetone (100 ml), followed by a solution of cupric chloride (2 g; 0·012 mol) in water (10 ml), was added. The mixture was then stirred at room temperature for 4 h, set aside overnight, neutralized with sodium carbonate (14·2 g), warmed for 3 h to 60°C, poured into water (400 ml) and extracted with chloroform. The extract was washed with water and dried over calcium chloride. Acidification of the aqueous layer afforded the unreacted acid (6·7 g). The organic layer was concentrated and the residue chromatographed on a column of silica gel with benzene as eluant. Following compounds were isolated: 4-nitrochlorobenzene (2·8 g); 2-(4-nitrophenyl)-1-(5-(4-nitrophenyl)-2-furyl)ethylene, m.p. 238—239°C (0·1 g), mass spectrum: M^+ 336 (100%), M + 1 (21·7%), M + 2 (6·7%); 2-(4-nitrophenyl)-1-(5-nitro-2-furyl)ethylene, m.p. 181—182°C (1·85 g; 14·2% based on the starting aniline).

Reaction of 4-Nitrobenzenediazonium Chloride with 2-Bromo-1-(5-nitro-2-furyl)ethylene

A mixture of 4-nitroaniline (3·45 g; 0·025 mol), conc. hydrochloric acid (15 ml) and water (8 ml) was diazotized with sodium nitrite (1·83 g) in water (10 ml) at 0—5°C. A solution of 2-bromo-1-(5-nitro-2-furyl)ethylene (5·45 g; 0·025 mol) in acetone (50 ml) was added, followed by a solution of cupric chloride (1 g; 0·006 mol) in water (5 ml). After stirring for 4 h at room temperature, the mixture was set aside overnight, neutralized with sodium carbonate (8·6 g), heated to 60°C for 3 h, poured into water (400 ml) and extracted with chloroform. The extract was washed with water, dried over calcium chloride, taken down and the residue was chromatographed on a column of silica gel in benzene. The chromatography afforded: 4-nitrochlorobenzene (1·54 g); 2-bromo-1-(5-nitro-2-furyl)ethylene (3·58 g); 2-(4-nitrophenyl)-1-(5-(4-nitrophenyl)-2-furyl)-ethy lene (0·11 g); and 2-(4-nitrophenyl)-1-(5-nitro-2-furyl)ethylene (0·94 g; 14·5%).

Reaction of 4-Ethoxycarbonylbenzenediazonium Tetrafluoroborate with 2-Bromo-1-(5-nitro-2-furyl)ethylene

A solution of 2-bromo-1-(5-nitro-2-furyl)ethylene (2·18 g; 0·01 mol) in acetone (10 ml), followed by a solution of cupric chloride (0·2 g; 0·0012 mol) in water (5 ml), was added to a solution of the diazonium salt (2·64 g; 0·01 mol) in acetone (40 ml). After stirring at room temperature for 4 h and standing overnight, the mixture was neutralized with sodium carbonate (3·5 g), heated to 60°C for 3 h, poured into water (100 ml) and extracted with ether. The extract was dried over calcium chloride, concentrated and chromatographed on a column of silica gel in chloroform, yielding: 2-bromo-1-(5-nitro-2-furyl)ethylene (0·98 g) and 2-(4-ethoxycarbonylphenyl)-1-(5-nitro-2-furyl)ethylene (0·87 g; 30·4%), m.p. 167—169°C. For $C_{15}H_{13}NO_5$ (287·3) calculated: 4·87% N; found: 4·69% N.

Photoreaction of 4-Nitrobenzenediazonium Tetrafluoroborate or 4-Ethoxycarbonylbenzenediazonium Tetrafluoroborate with 3-(5-Nitro-2-furyl)-2-propenoic Acid

A mixture of the diazonium salt (25 mmol), olefin (25 mmol), cupric chloride (40 mg; 0·3 mmol), lithium chloride (60 mg; 1·5 mmol), 2M-HCl (10 ml) and acetonitrile (100 ml) was saturated with nitrogen for 30 min and then irradiated with a medium-pressure mercury lamp in an all-glass apparatus until no diazonium salt was detected (alkaline solution of β-naphthol). The mixture was concentrated to 1/4 of its original volume, mixed with acetone (400 ml), neutralized with sodium carbonate (6·2 g), kept at 60°C for 3 h and filtered. The filtrate was taken down and the residue chromatographed on a column of silica gel in benzene, affording 1·07 g (16·5%) of 2-(4-nitrophenyl)-1-(5-nitro-2-furyl)ethylene or 1·12 g (15·6%) of 2-(4-ethoxycarbonylphenyl)-1-(5-nitro-2-furyl)ethylene.

Photoreaction of 4-R-Benzenediazonium Tetrafluoroborate with 2-Bromo-1-(5-nitro-2-furyl)ethylene (R = H, CH_3, OCH_3, $COOC_2H_5$)

The reaction was carried out as described in the preceding experiment and gave the corresponding products in the following yields: 2-phenyl-1-(5-nitro-2-furyl)ethylene (0·63 g; 11·8%); 2-(4-methylphenyl)-1-(5-nitro-2-furyl)ethylene (0·76 g; 13·3%); 2-(4-methoxyphenyl)-1-(5-nitro-2-furyl)ethylene (1·22 g; 19·9%); 2-(4-ethoxycarbonylphenyl)-1-(5-nitro-2-furyl)ethylene (1·18 g; 16·5%).

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