SYNTHESIS OF TRISUBSTITUTED ETHYLENES DERIVED FROM 5-NITRO-2-FURYLNITROMETHANE*

Iva Sroková, Adolf Jurášek, Miloslava Dandárová and Jaroslav Kováč

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

1-Nitro-1-(5-nitro-2-furyl)-2-(X-phenyl)ethylenes, where X = H, 4-CH₃, 4-OCH₃, 4-NO₂, 4-CN, 4-NHCOCH₃, 4-Cl, 4-N(CH₃)₂, 2-F, 2-OCH₃ and 2-NO₂, were prepared by condensation of 5-nitro-2-furylnitromethane (*A*) with aromatic aldehydes in a mixture of acetic acid and benzene, catalysed by ammonium acetate, or by reaction of *A* with azomethine of the corresponding aldehyde in acetic acid. The products have *E*-configuration and are formed by a *syn*-elimination reaction. Their IR, UV and ¹H-NMR spectra are interpreted.

The acidic character of hydrogens in nitromethane and its analogues has been widely utilised for synthetic purposes[1]. Condensation of these compounds with substituted furaldehydes affords furfurylidene derivatives which were used in the synthesis of corresponding amines[2-5] or in various addition reactions[6-8]. Phenylnitromethane reacts with 2-furaldehydes under formation of trisubstituted ethylenes. All these products contain the nitro group in the β-position to the furan ring[9-11]. In this paper we describe the synthesis of 5-nitro-2-furylnitromethane (*A*) which was used in the synthesis of 1-(5-nitro-2-furyl)-1-nitro-2-arylethylenes (*B*). In these trisubstituted ethylenes the nitro group, together with the 5-nitrofuran moiety, is bonded to the α-carbon.

The derivative *A* was synthesized starting from furfuryl alcohol which was nitrated to 5-nitrofurfuryl nitrate[12]. Treatment with an alkali metal halide afforded 5-nitrofurfuryl halide and this was transformed to *A* by the action of silver nitrite (Scheme 1). Satisfactory yields of *A* were obtained (44%) using 5-nitrofurfuryl bromide[13] in ether at low temperature[14,15]. Compound *A* forms smoothly the corresponding carbanion which reacts with aromatic aldehydes (procedure 1) or azomethines (procedure 2) to give compounds *B* according to Scheme 2 (ref.[16]). As seen from Table I, procedure 2 afforded substantially higher yields (41–84%) than procedure 1 (26–30%). However, derivatives containing electron-donating substituents were prepared by the procedure 2 only in negligible yields. All the synthesized compounds are yellow, except the 4-dimethylamino derivative *VI* which has a deep red colour.

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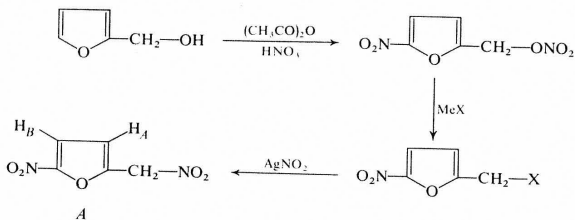
where Me = Na, K
and X = Br, I

SCHEME 1
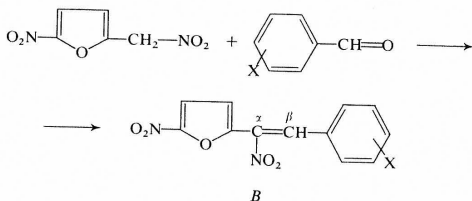
SCHEME 2

The UV spectra of most of the compounds (Table II) exhibit two absorption bands in the regions 275—216 nm and 318—298 nm which can be ascribed to the electronic transitions in the furan[17] and benzene[18] nuclei. The derivatives $III-VI$ with oxygen- or nitrogen-containing substituents attached to the benzene ring exhibit another band which in the case of the dimethylamino derivative VI is in the visible region at 460 nm (Fig. 1). One can assume that this compound exists in the quinoid structure C. The spectra of other derivatives exhibit no absorption band in this region; this indicates
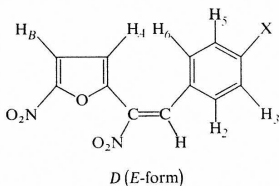

D (*E*-form)

TABLE I

Properties and Analytical Data of the Synthesized Compounds

Compound	M.p., °C (yield, %)	Formula (mol. w.)	Calculated/Found		
			% C	% H	% N
I H	139—141 (30)	$C_{12}H_8N_2O_5$ (260·2)	55·50 55·35	3·10 3·11	10·74 10·65
II 4-CH$_3$	137—139 (26)	$C_{13}H_{10}N_2O_5$ (271·1)	57·62 57·56	3·69 3·78	10·33 9·81
III 4-OCH$_3$	155—157 (28)	$C_{13}H_{10}N_2O_6$ (287·1)	54·30 53·88	2·44 2·45	9·76 9·50
IV 2-OCH$_3$	130—131 (25)	$C_{13}H_{10}N_2O_6$ (287·1)	54·30 54·10	2·44 2·60	9·76 9·53
V 4-NHCOCH$_3$	200/^{a} (47)	$C_{14}H_{11}N_3O_5$ (317·2)	53·00 52·83	3·50 3·33	13·25 13·18
VI 4-N(CH$_3$)$_2$	201—203 (26)	$C_{14}H_{13}N_3O_5$ (303·3)	55·50 55·90	4·33 4·32	13·88 13·80
VII 2-F	133—134 (50)	$C_{12}H_7N_2O_5F$ (278·2)	51·80 51·75	2·52 2·45	10·05 9·92
VIII 4-Cl	151—153 (41)	$C_{12}H_7ClN_2O_5$ (294·6)	48·90 48·75	2·38 2·24	9·50 9·31
IX 4-CN	178—180 (84)	$C_{13}H_7N_3O_5$ (285·2)	54·80 54·70	2·46 2·46	14·73 14·72
X 4-NO$_2$	171—172·5 (51)	$C_{12}H_7N_3O_7$ (305·2)	47·25 47·23	2·35 2·37	13·76 13·68
XI 2-NO$_2$	111—112 (69)	$C_{12}H_7N_3O_7$ (305·2)	47·25 47·11	2·35 2·25	13·76 13·54

^{a} Decomposition.

FIG. 1

UV Spectra of *a* 1-Nitro-1-(5-nitro-2-furyl)-
-2-(4-nitrophenyl)ethylene, *b* 1-Nitro-1-(5-
-nitro-2-furyl)-2-(4-dimethylaminophenyl)-
ethylene, *c* 1-Nitro-1-(5-nitro-2-furyl)-2-phe-
nylethylene
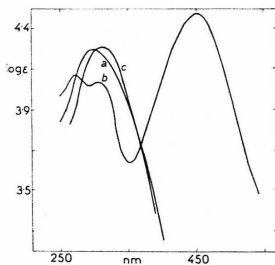
that these compounds are not entirely planar. The conjugation can be inhibited by rotation of the 5-nitro-2-furan and aryl moieties from the double bond plane, caused by the bulky nitro group.

The structure of the compounds $I - XI$ was confirmed by IR and ^{1}H-NMR spectroscopy (Table II and III). The IR spectra exhibit medium absorption bands $\nu(C=C)$ in the region $1670 - 1645$ cm^{-1}. Electron donating substituents (CH_3, OCH_3, $N(CH_3)_2$) in the *para*-position of the benzene ring shift these bands to lower wavenumbers whereas electron accepting groups (NO_2, CN) cause an opposite shift. All compounds except of the derivative VI exhibit two $\nu(NO_2)$ bands in the regions

TABLE II

Ultraviolet (nm) and Infrared (cm^{-1}) Spectra of the Synthesized Compounds

Compound	λ_{max}, (log ε)			$\nu_s(COC)$	$\nu_s(NO_2)$	$\nu_{as}(NO_2)$	$\nu(C=C)$
I	— —	310 (4·30)	228 (4·00)	1 025	1 330 1 355	1 545	1 670
II	— —	318 (4·19)	231 (4·04)	1 030	1 330 1 355	1 558	1 668
III	363 (4·22)	310 (4·13)	238 (4·09)	1 027	1 310 1 355	1 545	1 665
IV	362 (4·10)	304 (4·02)	— —	1 028	1 330 1 355	1 555	1 665
V^a	370 (4·29)	310 (4·11)	246 (4·09)	1 023	1 315 1 358	1 535	1 683
VI	460 (4·48)	310 (4·22)	275 (4·26)	1 025	— 1 355	1 545	1 655
VII	— —	307 (4·26)	— —	1 028	1 332 1 355	1 550	1 670
$VIII$	— —	312 (4·33)	230 (4·17)	1 023	1 332 1 353	1 550	1 670
IX	— —	298 (4·29)	234 (4·21)	1 028	1 332 1 350	1 555	1 675
X	— —	298 (4·24)	216 (4·08)	1 028	1 332 1 355	1 560	1 678
XI	— —	312 (4·11)	— —	1 029	1 340 1 360	1 550	1 655

^{a} IR spectra measured in KBr.

$1340-1310$ cm^{-1} and $1360-1350$ cm^{-1}; one of them is due to the NO$_2$ group at the α-ethylenic carbon and the other due to the NO$_2$ group attached to the furan nucleus. From the fact that the derivative *VI* exhibits only one band at 1355 cm^{-1} we can deduce that the lower wavenumber band corresponds to the nitro group bonded to the furan ring, since in *VI* the character of the NO$_2$ group is changed by transition into the quinoid structure.

The ^{1}H-NMR spectra (Table III) show that the substituent *X* in the *para*-position of the benzene ring does not practically effect the ethylenic proton signal. Such effect was reported for trisubstituted sulphur derivatives of 5-nitrofuran chalcones[19] where it was identified as a linear dependence of σ_p Hammett constants on δ(C=CH). The absence of such an effect in the case of our compounds can be explained by the above-mentioned non-planarity of these systems in which no mesomeric substituent effects can occur.

According to the ^{1}H-NMR spectra (Table III), the condensation of benzaldehydes with the compound A affords only one geometric isomer, *i.e.* the reaction is stereospecific. This was confirmed by taking the spectra not only of the purified compounds but also of the crude reaction products. The positions of the ethylenic proton signal, calculated from the additive increments[20,21] (the increment value of 5-nitrofuran nucleus was approximated by that for aryl) are as follows: *E* isomer 8·23 ppm *Z* isomer 7·45 ppm. Comparison of these values with the experimental value δ(C==CH) (8·47 ppm) shows that the synthesized compounds have the *E* configuration.

TABLE III
^{1}H-NMR Spectra of the Synthesized Compounds (δ, ppm; J, Hz)

Compound	—CH==	H$_A$[a]	H$_B$[a]	J_{AB}	H$_2$, H$_6$	H$_3$, H$_6$	$J_{2,3}$[b]
I	8·47	6·81	7·40	3·8	(7·11—7·55)[c]		—
II	8·48	6·80	7·41	3·7	7·15	7·13	9·2
III	8·45	6·81	7·42	3·8	7·18	6·85	8·9
IV	8·81	6·77	7·36	3·8	(6·80—6·98; 7·36—7·55)[c]		
V	8·59	7·17	7·80	3·8	7·32	7·64	8·9
VI	8·43	6·80	7·42	3·8	7·06	6·56	9·0
VII	8·58	6·87	7·38	3·9	(6·98—7·18; 7·36—7·58)[c]		
VIII	8·42	6·84	7·41	3·8	7·35	7·17	9·0
IX	8·42	6·90	7·40	3·8	7·36	7·67	9·0
X	8·46	6·92	7·40	3·9	7·44	8·23	9·0
XI	8·75	6·88	7·22	3·8	[d]	[d]	

[a] Doublet; [b] $J_{2,3} = J_{5,6}$; [c] multiplet of the aromatic protons; [d] H$_3$ 8·33, H$_4$ 7·26, H$_5$ 7·66.

The formation of E isomers as the sole products can be explained on the basis of steric effects operating in the reaction of the carbanion formed from the compound A with the carbonyl or azomethine group of the other reaction component. In principle, we can assume two pathways leading to the product B (Scheme 3). Transition state I

C

I

II
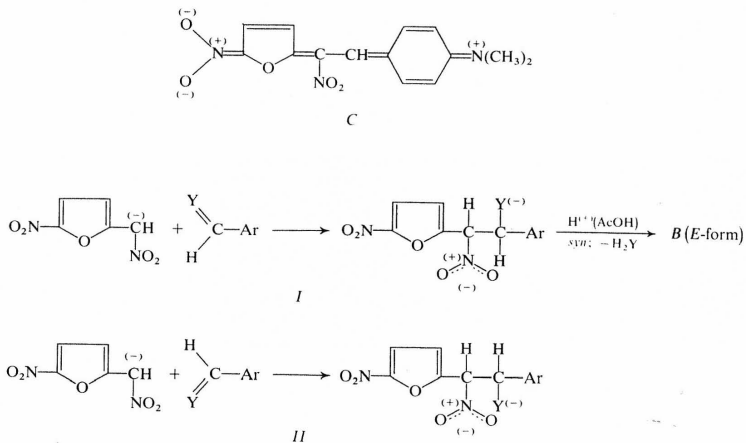
$Y = O, N; H_2Y = H_2O, C_4H_9NH_2$

SCHEME 3

is energetically as well as sterically better off than the transition state II since in I the bulky NO_2 group with the negative charge on its two oxygens is antiperiplanar to the bulky and negatively charged oxygen or nitrogen. An opposite situation is in the case of the transition state II. If a compound of E configuration should arise, the water (procedure 1) or butylamine (procedure 2) must be removed by syn-elimination, analogously to the elimination of water in the condensation reaction of 5-nitrofurfuryl sulphones with aromatic aldehydes[22].

EXPERIMENTAL

The yields, melting points and analytical data for the synthesized compounds are given in Table I. The IR spectra were taken in the region $700-3800$ cm^{-1} on a UR-20 spectrophotometer (Zeiss, Jena), in saturated chloroform solutions (0·4 or 0·6 mm cells) or by the KBr technique (2 mg/l g

KBr). The instrument was calibrated by a polystyrene foil, accuracy ± 1 cm^{-1}. Chloroform was passed through a silica gel column in order to remove ethanol. The electronic absorption spectra were measured in $5 \cdot 10^{-5}$ mol l^{-1} dioxane solutions in the region $200-800$ nm on a Specord UV VIS (Zeiss, Jena) instrument in 1 cm cells (Table II). ^{1}H-NMR spectra were taken in CDCl$_3$ on a BS-487C (80 MHz, Tesla, Brno) instrument; δ scale, tetramethylsilane as internal standard.

5-Nitro-2-furylnitromethane (A)

An ethereal solution of 5-nitrofurfuryl bromide (20·6 g; 0·1 mol) was added at 0°C in the course of 1 h to a stirred suspension of anhydrous silver nitrite (46·2 g; 0·3 mol) in ether (300 ml) and the mixture was stirred at 0°C for 24 h. The excess silver nitrite was filtered and the filtrate was taken down *in vacuo*, yield 7·6 g (44·2%), m.p. 78—80°C. The structure A was proved by IR, UV and ^{1}H-NMR data. IR spectrum, cm^{-1}: 3150, 1585, 1560, 1520, 1405, 1360, 1315, 1130, 890; UV spectrum: $\lambda_{max} = 304$ nm, log $\varepsilon = 4·017$; ^{1}H-NMR spectrum (ppm): 5·53, s, 2 H (CH$_2$), 6·85, d, 3·7 Hz (H$_A$), 7·33, d, 3·7 Hz (H$_B$). For C$_5$H$_4$N$_2$O$_5$ (172·9) calculated: 34·78% C, 2·34% H, 16·22% N; found: 34·80% C, 2·36% H, 16·14% N.

Condensation

Procedure 1 (compounds $I-IV$, VI): A solution of the corresponding aldehyde (0·01 mol) in benzene (10 ml) was added to a solution of the compound A (1·72 g; 0·01 mol) in benzene (30 ml). Acetic acid (5 ml) and ammonium acetate (0·1 g) were added and water was removed by azeotropic distillation during 8—10 h. The mixture was poured into ice-cold water (about 100 ml), the separated benzene layer was shaken twice with a 5% sodium hydrogen carbonate solution, dried over sodium sulphate and the solvent was distilled off *in vacuo*.

Procedure 2 (compounds V, $VII-XI$): Azomethine, prepared from the corresponding aldehyde (0·01 mol) and n-butylamine (0·01 mol)[9], was added at room temperature to a solution of the compound A (0·01 mol) in concentrated acetic acid (10—15 ml). After several minutes a crystalline compound began to separate. Upon standing for 24 h the product was filtered and was crystallized from acetic acid.

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