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Nitration of Some 3-(2-Furyl)-2-propenones with Dinitrogen Tetraoxide

A. I. Sitkin and V. I. Klimenko

Kazan State Technological University, ul. K. Marksa 68, Kazan, 420015 Tatarstan, Russia

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Abstract—Nitration of 3-(2-furyl)-2-propenones with dinitrogen tetraoxide leads to the corresponding 3-(4-nitro-2-furyl)-2-propenones. If the furyl group contains a substituent in position *5*, the nitration occurs at the side chain to afford 3-(5-R-2-furyl)-2-nitro-2-propenones.

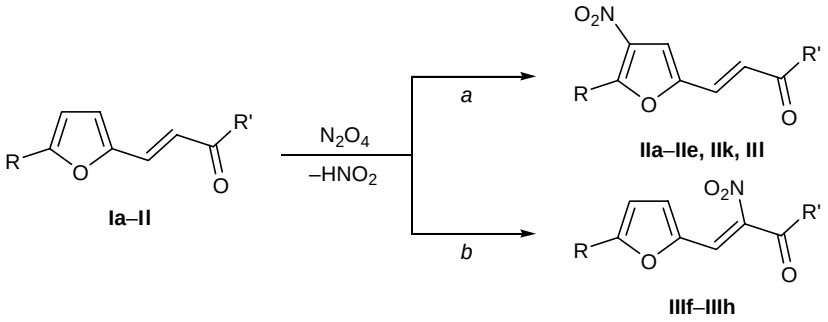
3-(5-Nitro-2-furyl)-2-propenones are known to exhibit strong bactericidal and bacteriostatic activity [1]. These compounds are usually prepared by crotonization of 5-nitrofuraldehyde with appropriate ketones [1] or by reaction of 3-(2-furyl)-2-propenones with nitric acid in acetic anhydride [2]. The goal of the present work was to synthesize new isomeric nitro compounds of the above series by reaction of equimolar amounts of liquid dinitrogen tetraoxide with 3-(2-furyl)-2-propenones **Ia**–**Ij** in diethyl ether at reduced temperature.

We have found that the nitration products of furylpropenones **Ia**–**Ie** having no substituent in the furan ring are the corresponding 3-(4-nitro-2-furyl)-2-propenones **IIa**–**IIe** (Scheme 1). However, treatment with dinitrogen tetraoxide of compounds **If**–**Ih** containing a substituent in position *5* of the heteroring leads to formation of products with a nitro group in the side chain, substituted 3-(5-R-2-furyl)-2-nitro-2-propenones **IIIf**–**IIIh**. The nitration of 5-bromo- and 5-iodofuryl derivatives **Ii** and **Ij** also affords unsaturated dinitroketone **IIIf** as a result of replacement of the halogen atom in the furan ring by nitro group.

According to published data [3], nitration of unsaturated compounds with dinitrogen tetraoxide under analogous conditions (equimolar amounts of the reactants, diethyl ether, cooling) follows a radical mechanism and occurs at the most spatially accessible carbon atom. Therefore, the observed reaction pathways (*a* and *b* in Scheme 1) indicate that the most spatially accessible reaction centers in furylpropenones **Ia**–**Ij** are C^4 in the furan ring and the α-carbon atom (with respect to the carbonyl group). The side-chain carbon atom in molecules **Ia**–**Ie** is partially shielded by bulky acyl groups (COC_6H_4R), and the nitration follows mainly pathway *a* provided that no substituent is present in position *5* of the furan ring. Otherwise (compounds **If**–**Ij**), position *4* in the heteroring becomes less accessible, and the reaction occurs according to pathway *b*.

It was reasonable to presume that the absence of bulky acyl groups and substituents in the furan ring

Scheme 1.



I, **II**, R = H, R' = Ph (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**), 4-MeC_6H_4 (**d**), 4-$MeOC_6H_4$ (**e**), OH (**k**), H (**l**); **I**, **III**, R = NO_2, R' = Ph (**f**), Me (**g**), R = R' = Me (**h**); **I**, R' = Ph, R = Br (**i**), I (**j**).

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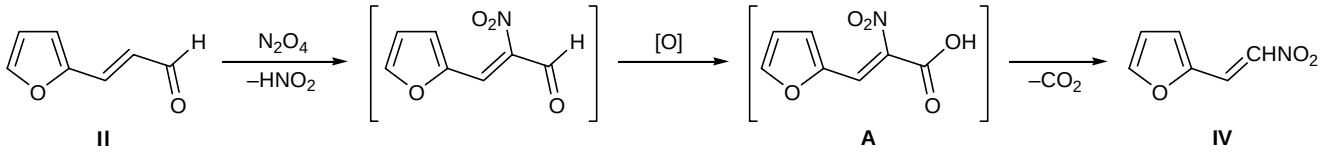
Scheme 2.



should favor nitration of compounds **Ik** and **Il** with dinitrogen tetraoxide at both reaction centers. In fact, by reacting 3-(2-furyl)acrylic acid (**Ik**) and 3-(2-furyl)-acrylaldehyde (**Il**) with N_2O_4 we isolated in each case two nitro derivatives: 4-nitrofuryl **IIk** and **Ill** (pathway *a*) and 1-(2-furyl)-2-nitroethylene (**IV**); the latter product was identified by comparison with an authentic sample [4]. The formation of nitroalkene **IV** from furylacrylic acid **Ik** may be explained by easy decarboxylation of intermediate 3-(2-furyl)-2-nitroacrylic acid (**A**) which is formed along pathway *b*. In the nitration of aldehyde **Il**, the primary nitration product, 3-(2-furyl)-2-nitro-2-propenal (pathway *b*), is likely to be readily oxidized to acid **A** whose decarboxylation yields nitroalkene **IV** (Scheme 2).

The IR spectra of initial compounds **I** indicate the existence of conjugation between the double bond π-electron systems in their molecules: $\nu_{C=C}$ 1648–1605, $\nu_{C=O}$ 1680–1655 cm^{-1}. In the IR spectra of nitro derivatives **II** and **III**, the carbonyl absorption band is displaced by 5–20 cm^{-1} toward higher frequencies; this means that the conjugation between the carbonyl group and double C=C bond weakens. The C=C absorption frequency also increases (by 3–12 cm^{-1}). In addition, the IR spectra of **II** and **III** contain strong absorption bands due to asymmetric and symmetric vibrations of the conjugated nitro group in the regions 1545–1525 and 1375–1350 cm^{-1}, respectively. The furan ring gives rise to characteristic absorption bands at 3155–3120, 1035–1015, and 890–868 cm^{-1}. The bands in the regions 1230–1070 and 850–812 cm^{-1} correspond to in-plane and out-of-plane bending vibrations of the aromatic C–H bonds. Stretching vibrations of the latter appear at 3072–3010 cm^{-1}. Compounds containing methoxy (2845, 1255 cm^{-1}) or methyl groups (2870–2856, 1482–1460 cm^{-1}) and C–Cl (740–700 cm^{-1}) or C–Br bonds (650, 560 cm^{-1}) showed in the IR spectra the corresponding absorption bands.

The ^{1}H NMR spectra of initial compounds **Ia**–**Ie** and **Ik** in acetone-d_6 are characterized by the presence of two doublets from the *trans*-ethylene protons (2-H and 3-H, *AA*' system) with a coupling constant ^3J of 16 Hz and signals from protons in the furan ring: doublets at δ 6.90–7.16 (3'-H) and 7.70–7.82 ppm (5'-H) and a quartet from 4'-H ($J_{3,4} \approx 3.5$, $J_{4,5} \approx 1.8$ Hz). All protons in the spectra of 4-nitrofuryl derivatives **IIa**–**IIe** and **IIk** resonate in a weaker field due to deshielding by the nitro group, the largest downfield shifts being observed for the 3'-H and 5'-H signals (Δδ 0.51–0.74 and 1.01–1.13 ppm, respectively). The spectra lack quartet signal corresponding to 4'-H in the initial compounds, and the 3'-H and 5'-H signals appear as singlets rather than doublets. The side-chain olefinic protons, as in the spectra of the initial compounds, give rise to an *AA*' system with the same coupling constant ($^3J_{trans}$ = 16 Hz). The aldehyde proton signal and that from 3-H in the spectra of **Il** and **Ill** are doublets, and the 2-H signal is a quartet. *ortho*- and *meta*-Aromatic protons in **IIb**–**IIe** give doublets with coupling constants of 8.0–8.5 Hz, and aromatic protons in **IIa** and **IIIf** appear as multiplets. Signals from the methyl group protons were also present in the spectra of ketones **IId**, **IIe**, **IIIg**, and **IIIh**.

The ^{1}H NMR spectra of **III** lack signal corresponding to 2-H in initial ketones **If**–**Ij** [δ, ppm: 6.80–7.58 d (2-H), 7.12–7.92 d (3-H), $^3J_{2,3} \approx 16$ Hz], while signals from the other protons are located in a weaker field. The 3-H proton in **III** is the most deshielded (δ 0.45–0.49 ppm); it appears as a singlet, for there is no proton in the neighboring position (C^2). The furan ring protons (3'-H and 4'-H) give rise to two doublets.

In going from solutions of compounds **II** and **III** in acetone-d_6 to solutions in DMSO-d_6, signals from all protons in their molecules shift downfield. The largest shift for compounds **II** was observed for 5'-H (Δδ 0.52–0.62 ppm); the other signals were displaced downfield to a lesser extent ($\Delta\delta_{3\text{-H}}$ 0.19–0.30, $\Delta\delta_{2\text{-H}}$ 0.17–0.30, $\Delta\delta_{1\text{-H}}$ 0.13–0.40, $\Delta\delta_{o\text{-H}}$ 0.17–0.29, $\Delta\delta_{m\text{-H}}$ 0.22–0.26 ppm). Compounds **III** were also characterized by large and positive Δδ values (0.25–0.47 ppm) for all protons. It should be noted that the difference in the chemical shifts of protons in **II** and **III**, on the one hand, and initial compounds, on the other, are larger in DMSO-d_6 than in acetone-d_6. For example, Δδ values in DMSO for 5'-H in **IIa**, **IIb**, and **IId**, as compared to **Ia**, **Ib**, and **Id** (δ 8.05–8.15 ppm, d), range from 1.20 to 1.41 ppm, and for 3-H in **III**, from 0.57 to 0.67 ppm (**If**–**Ih**, $\delta_{3\text{-H}}$ 7.47–8.09 ppm, DMSO-d_6).

According to [5], ketone **Ia** exists mainly as *syn-trans-s-cis* conformer, while aldehyde **Il** is characterized by *syn-trans-s-trans* conformation. We have determined the configuration of compounds **Ia**, **Ib**, **Il**, **IIa**, **IIb**, and **IIl**. The coupling constant for the olefinic protons in the ^{1}H NMR spectra is equal to ~16 Hz, indicating *trans*-configuration of the double bond. The greater intensity of the $\nu_{C=C}$ band as compared to $\nu_{C=O}$ ($\nu_{C=O}/\nu_{C=C}$ = 0.3–0.5) in the IR spectra of ketones **Ia**, **Ib**, **IIa**, and **IIb** suggests that the conjugated carbonyl group and ethylene moiety are arranged *s-cis* [5]. The intensity ratio of the C=O and C=C absorption bands in the IR spectra of aldehydes **Il** and **IIl** is equal to 2.5, which is typical of transoid orientation of the corresponding groups [6].

The fractions of the *syn* and *anti* isomers of *trans-s-cis*-ketones **Ia**, **Ib**, **IIa**, and **IIb** and *trans-s-trans*-aldehydes **Il** and **IIl** were estimated by comparing the experimental dipole moments with those calculated by the vector additivity scheme for the corresponding conformations (see table). The calculations were performed using the formula $\mu = (m_x^2 + m_y^2)^{1/2}$, where m_x and m_y are, respectively, the sums of the projections of the bond dipole moments on the *x* and *y* axes. The coordinate system was set in such a way that the *x* axis passed through positions *2* and *5* of the furan ring, and the *y* axis, through position *3*. The required parameters of 2-substituted furan ring and dipole moments of particular groups and bonds in molecules **Ia**, **Ib**, **Il**, **IIa**, **IIb**, and **IIl** were taken from [5]. The dipole moment of the nitro group in position *4* of the furan ring was assumed to be 4.01 D (i.e., as in nitrobenzene [7]), and the moment of chlorine in aromatic ring was taken equal to 1.59 D [7].

As follows from the data collected in table, both *s-cis*-propenones **Ia** and **Ib** and *s-trans*-acrolein **Il** in solution exist mainly as *syn* conformers. However, introduction of a nitro group into the furan ring shifts the conformational equilibrium. The experimental

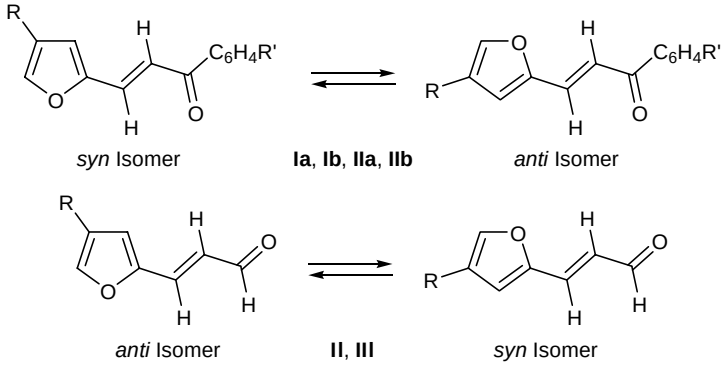
Dipole moments of compounds **Ia**, **Ib**, **Il**, **IIa**, **IIb**, and **IIl**

Comp. no.	μ_{exp}, D	μ_{calc}, D	
		syn isomer	*anti* isomer
Ia	3.59	3.55	2.73
IIa	3.82	1.75	4.77
Ib	3.41	2.97	2.59
IIb	3.07	1.04	3.22
Il	4.58	4.09	3.26
IIl	2.54	1.80	5.14

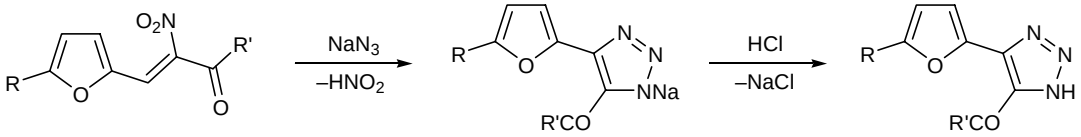
dipole moments of ketones **IIa** and **IIb** and aldehyde **IIl** occupy an intermediate place between the values calculated for their *syn* and *anti* conformers; therefore, these compounds give rise to equilibrium mixtures of the *syn* and *anti* conformers. Using the formula $\mu = (1 - x)\mu_1^2 + x\mu_2^2$, we obtained the following fractions of the *syn* conformer: **IIa**, 0.41; **IIb**, 0.10; **IIl**, 0.86. The formation of an equilibrium mixture of *syn* and *anti* conformers of the above compounds may be rationalized in terms of electron-acceptor effect of the nitro group, which weakens π-electron density transfer in the conjugated system furan ring–ethylene fragment–carbonyl group from the former to the latter. As a result, rotation of the furan ring about the C^3–$C^{2'}$ bond becomes possible.

The experimental dipole moments of nitro ketones **IIIf**–**IIIh** in which the nitro group is located at the side-chain double bond are 5.04, 4.96, and 5.79 D, respectively. These values considerably exceed those found for initial compounds **If**–**Ih** having a planar structure (3.48, 3.72, and 4.34 D, respectively). Presumably, the nitro group in molecules **III** is forced out from the plane of the rest of the molecule, thus ruling out or strongly reducing its conjugation with the furan ring and carbonyl group.

Carbonyl compounds **II** and **III** can readily be converted into the corresponding 2,4-dinitrophenylhydrazones **V**. The IR spectra of the latter lack absorption



Scheme 3.



IIIf–IIIh **VIf–VIh**

due to carbonyl stretching vibrations, but bands belonging to vibrations of the C=N (1615 cm^{-1}) and N–H bonds (3450, 3400, and 1315 cm^{-1}) are present. Treatment of ketones **III** with sodium azide in a dipolar aprotic (DMF) or protic solvent (EtOH) afforded the corresponding 5-acyl-4-(2-furyl)-1*H*-1,2,3-triazoles **VI**. The reaction is likely to occur via [3+2]-cycloaddition of azide ion at the double bond and elimination of nitrous acid molecule (Scheme 3). Compounds **VI** showed in the IR spectra absorption bands at 1690–1650 (C=O), 3200–3100 (NH), 1530–1520 and 1360–1350 (NO_2), 1020–990 (triazole ring), 1500, 1030, 890, 775 (furan), 1380 (Me), and 1600, 1248–1240, 1186–1155 cm^{-1} (arom.). Unlike initial compounds **III**, the ^{1}H NMR spectra of **VI** contained no signals assignable to olefinic proton. 4-Nitrofuryl derivatives **II** failed to react with sodium azide; presumably, the olefinic double bond in these compounds is insufficiently electrophilic.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer from samples dispersed in mineral oil. The intensity ratio of the $\nu_{C=O}$ and $\nu_{C=C}$ bands was determined by cutting and weighing the corresponding peaks. The ^{1}H NMR spectra were recorded from solutions in acetone-d_6 on a Varian CFT-20 spectrometer (80 MHz) and in DMSO-d_6 on a Tesla BS 487C spectrometer (80 MHz). The chemical shifts were measured relative to tetramethylsilane. The dipole moments were determined by the Debye technique from dilute solutions [7] in dioxane at 25±0.1°C using an ON-302 precision dielcometer; the solvent was purified by the procedure described in [8]. The compounds under study were recrystallized until constant melting point and were dried under reduced pressure. The purity of the products was checked by TLC on Silufol UV-254 plates using benzene as eluent; spots were visualized under UV light. Initial compounds **Ia**–**Il** were synthesized and purified by the procedures reported in [9].

Nitro compounds II and III (*general procedure***).** A solution of 10 mmol of compound **Ia**–**Ie** or **Ih** in 50 ml of diethyl ether was cooled to –15°C, 10 mmol of dinitrogen tetraoxide was added, and the mixture was stirred for 2 h at that temperature and poured onto 100 g of finely crushed ice. After 3 h, the organic phase was separated, and the solvent was evaporated. The residue was washed in succession with water and alcohol, and recrystallized from appropriate solvent. We thus isolated nitro ketones **IIa**–**IIe** and **IIIh**. Following the same procedure, in the reaction of aldehyde **Il** with N_2O_4, apart from 4-nitrofuryl derivative **IIl**, we isolated by fractional crystalization from carbon tetrachloride 14% of furylnitroethylene **IV** with mp 74°C [4]. Compound **IV** was also isolated in 18% yield (mp 74–75°C, from CCl_4) in addition to nitro acid **IIk** in the nitration of 3-(2-furyl)acrylic acid (**Ik**). Dinitro ketone **IIIf** was synthesized from compound **If**, **Ii**, or **Ij** and dinitrogen tetraoxide at a reactant molar ratio of 1:4; the reaction mixture was stirred for 3 h at 0°C); yield 47, 32, and 33%, respectively. Likewise, dinitropropenone **IIIg** was synthesized from compound **Ig** using 2 equiv of N_2O_4 (temperature 17°C).

3-(4-Nitro-2-furyl)-1-phenyl-2-propenone (IIa). Yield 15%, mp 157–158°C (from EtOH). IR spectrum, ν, cm^{-1}: 1620 (C=C); 1680 (C=O); 1540, 1368 (NO_2). ^{1}H NMR spectrum, δ, ppm: in acetone-d_6: 7.46 d (1H, 2-H, J = 15.8 Hz), 7.56 s (1H, 1-H), 7.65–8.12 m (5H, H_{arom}), 7.82 d (1H, 3-H, J = 15.8 Hz), 8.83 s (1H, 5'-H); in DMSO-d_6: 7.73 d (1H, 2-H, J = 16.0 Hz), 7.87–8.29 m (5H, H_{arom}), 7.95 s (1H, 1-H), 8.01 d (1H, 3-H, J = 16.0 Hz), 9.35 s (1H, 5'-H). Found, %: C 64.46; H 3.90; N 5.82. $C_{13}H_9NO_4$. Calculated, %: C 64.14; H 3.70; N 5.76.

1-(4-Chlorophenyl)-3-(4-nitro-2-furyl)-2-propenone (IIb). Yield 14%, mp 190–191°C (from EtOH). IR spectrum, ν, cm^{-1}: 1620 (C=C); 1670 (C=O); 1530, 1370 (NO_2). ^{1}H NMR spectrum, δ, ppm: in acetone-d_6: 7.54 d (1H, 2-H, J = 15.8 Hz), 7.66 d (2H, *m*-H, J = 8.5 Hz), 7.69 s (1H, 1-H), 7.79 d (1H, 3-H, J = 15.8 Hz), 8.12 d (2H, *o*-H, J = 8.5 Hz), 8.84 s (1H, 5'-H); in DMSO-d_6: 7.80 d (1H, 2-H, J = 15.9 Hz), 7.92 d (2H, *m*-H, J = 8.0 Hz), 8.03 s (1H, 1-H), 8.09 d (1H, 3-H, J = 15.9 Hz), 8.41 d (2H, *o*-H, J = 8.0 Hz), 9.46 s (1H, 5'-H). Found, %: C 56.08;

H 2.92; Cl 13.03; N 5.16. $C_{13}H_8ClNO_4$. Calculated, %: C 56.23; H 2.90; Cl 12.78; N 5.04.

1-(4-Bromophenyl)-3-(4-nitro-2-furyl)-2-propenone (IIc). Yield 11%, mp 189–190°C (from EtOH). IR spectrum, ν, cm^{-1}: 1608 (C=C); 1660 (C=O); 1525, 1367 (NO_2). ^1H NMR spectrum (acetone-d_6), δ, ppm: 7.52 s (1H, 1-H), 7.53 d (1H, 2-H, *J* = 15.6 Hz), 7.74 d (2H, *m*-H, *J* = 8.7 Hz), 7.77 d (1H, 3-H, *J* = 15.6 Hz), 8.03 d (2H, *o*-H, *J* = 8.7 Hz), 8.77 s (1H, 5'-H). Found, %: C 48.31; H 2.57; Br 24.90; N 4.24. $C_{13}H_8BrNO_4$. Calculated, %: C 48.47; H 2.50; Br 24.80; N 4.34.

3-(4-Nitro-2-furyl)-1-(4-tolyl)-2-propenone (IId). Yield 29%, mp 148–149°C (from EtOH). IR spectrum, ν, cm^{-1}: 1620 (C=C); 1675 (C=O); 1536, 1365 (NO_2). ^1H NMR spectrum, δ, ppm: in acetone-d_6: 2.43 s (3H, Me), 7.38 d (2H, *m*-H, *J* = 8.0 Hz), 7.42 d (1H, 2-H, *J* = 15.6 Hz), 7.52 s (1H, 1-H), 7.81 d (1H, 3-H, *J* = 15.6 Hz), 8.02 d (2H, *o*-H, *J* = 8.0 Hz), 8.80 s (1H, 5'-H); in DMSO-d_6: 7.60 d (2H, *m*-H, *J* = 8.0 Hz), 7.65 s (1H, 1-H), 7.72 d (1H, 2-H, *J* = 15.0 Hz), 8.01 d (1H, 3-H, *J* = 15.0 Hz), 8.23 d (2H, *o*-H, *J* = 8.0 Hz), 9.35 s (1H, 5'-H). Found, %: C 65.58; H 4.47; N 5.71. $C_{14}H_{11}NO_4$. Calculated, %: C 65.36; H 4.31; N 5.44.

1-(4-Methoxyphenyl)-3-(4-nitro-2-furyl)-2-propenone (IIe). Yield 29%, mp 176–177°C (from benzene). IR spectrum, ν, cm^{-1}: 1620 (C=C); 1670 (C=O); 1545, 1370 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.85 s (3H, OMe), 7.45 d (2H, *m*-H, *J* = 8.4 Hz), 7.58 s (1H, 1-H), 7.90 d (1H, 2-H, *J* = 16.0 Hz), 8.11 d (1H, 3-H, *J* = 16.0 Hz), 8.49 d (2H, *o*-H, *J* = 8.4 Hz), 8.80 s (1H, 5'-H). Found, %: C 61.71; H 4.20; N 5.21. $C_{14}H_{11}NO_5$. Calculated, %: C 61.54; H 4.10; N 5.13.

3-(4-Nitro-2-furyl)acrylic acid (IIk). Yield 12%, mp 216–217°C (from EtOH). IR spectrum, ν, cm^{-1}: 1638 (C=C); 1690 (COO); 1530, 1367 (NO_2). ^1H NMR spectrum (acetone-d_6), δ, ppm: 6.50 d (1H, 2-H, *J* = 15.9 Hz), 7.43 s (1H, 1-H), 7.50 d (1H, 3-H, *J* = 15.9 Hz), 8.79 s (1H, 5'-H), 13.31 s (1H, COOH). Found, %: C 45.97; H 2.85; N 7.61. $C_7H_5NO_5$. Calculated, %: C 45.90; H 2.73; N 7.65.

3-(4-Nitro-2-furyl)-2-propenal (IIl). Yield 18%, mp 135–136°C (from CCl_4). IR spectrum, ν, cm^{-1}: 1634 (C=C); 1660 (C=O); 1530, 1370 (NO_2). ^1H NMR spectrum, δ, ppm: in acetone-d_6: 6.65 q (1H, 2-H, *J* = 16.1, 7.6 Hz), 7.53 s (1H, 1-H), 7.57 d (1H, 3-H, *J* = 16.1 Hz), 8.85 s (1H, 5'-H), 9.71 d (1H, CHO, *J* = 7.6 Hz); in DMSO-d_6: 6.82 q (1H, 2-H, *J* = 17.0, 7.0 Hz), 7.82 d (1H, 3-H, *J* = 17.0 Hz), 7.93 s (1H, 1-H), 9.38 s (1H, 5'-H), 9.89 d (1H, CHO, *J* = 7.0 Hz). Found, %: C 50.40; H 3.09; N 8.32. $C_7H_5NO_4$. Calculated, %: C 50.30; H 3.01; N 8.38.

2-Nitro-3-(5-nitro-2-furyl)-1-phenyl-2-propenone (IIIf). Yield 47%, mp 140–141°C (from AcOH). IR spectrum, ν, cm^{-1}: 1655 (C=C); 1680 (C=O); 1540, 1350 (NO_2). ^1H NMR spectrum, δ, ppm: in acetone-d_6: 7.45 d (1H, 3'-H, *J* = 3.8 Hz), 7.55 d (1H, 4'-H, *J* = 3.8 Hz), 7.64–8.08 m (5H, H_{arom}), 8.39 s (1H, 3-H); in DMSO-d_6: 7.55 d (1H, 4'-H, *J* = 3.8 Hz), 7.70 d (1H, 3'-H, *J* = 3.8 Hz), 7.87–8.22 m (5H, H_{arom}), 8.76 s (1H, 3-H). Found, %: C 54.38; H 2.83; N 9.80. $C_{13}H_8N_2O_6$. Calculated, %: C 54.18; H 2.79; N 9.72.

1-Methyl-2-nitro-3-(5-nitro-2-furyl)-2-propenone (IIIg). Yield 56%, mp 176–177°C (from AcOH). IR spectrum, ν, cm^{-1}: 1660 (C=C); 1693 (C=O); 1560, 1362 (NO_2). ^1H NMR spectrum, δ, ppm: in acetone-d_6: 2.58 s (3H, Me), 7.34 d (1H, 3'-H, *J* = 3.8 Hz), 7.63 d (1H, 4'-H, *J* = 3.8 Hz), 7.87 s (1H, 3-H); in DMSO-d_6: 7.65 d (1H, 3'-H, *J* = 4.0 Hz), 8.01 d (1H, 4'-H, *J* = 4.0 Hz), 8.34 s (1H, 3-H). Found, %: C 42.52; H 2.61; N 12.50. $C_8H_6N_2O_6$. Calculated, %: C 42.48; H 2.65; N 12.39.

1-Methyl-3-(5-methyl-2-furyl)-2-nitro-2-propenone (IIIh). Yield 24%, mp 158–159°C (from EtOH). IR spectrum, ν, cm^{-1}: 1625 (C=C); 1660 (C=O); 1540, 1375 (NO_2). ^1H NMR spectrum, δ, ppm: in acetone-d_6: 2.35 s (3H, 5'-CH_3), 2.45 s (3H, 1-CH_3), 6.39 d (1H, 4'-H, *J* = 3.8 Hz), 7.08 d (1H, 3'-H, *J* = 3.8 Hz), 7.57 s (1H, 3-H); in DMSO-d_6: 6.72 d (1H, 4'-H, *J* = 4.0 Hz), 7.43 d (1H, 3'-H, *J* = 4.0 Hz), 8.04 s (1H, 3-H). Found, %: C 55.35; H 4.67; N 7.21. $C_9H_9NO_4$. Calculated, %: C 55.38; H 4.62; N 7.18.

2,4-Dinitrophenylhydrazones V (*general procedure*). Aldehyde or ketone **II** or **III**, 1 mmol, was dissolved on heating in 10–15 ml of diethyl ether, and a hot solution of 1 mmol of 2,4-dinitrophenylhydrazine in 5–10 ml of alcohol acidified with concentrated hydrochloric acid (0.5–2 ml) was added. The mixture was heated for 10–40 min, and the precipitate was filtered off, washed in succession with water, alcohol, and diethyl ether, and recrystallized from appropriate solvent.

3-(4-Nitro-2-furyl)-1-phenyl-2-propenone 2,4-dinitrophenylhydrazone (Va). Yield 89%, mp 230–231°C (from benzene). Found, %: N 16.47. $C_{19}H_{13}N_5O_7$. Calculated, %: N 16.54.

1-(4-Chlorophenyl)-3-(4-nitro-2-furyl)-2-propenone 2,4-dinitrophenylhydrazone (Vb). Yield 75%, mp 199–200°C (from benzene). Found, %: Cl 7.68; N 15.23. $C_{19}H_{12}ClN_5O_7$. Calculated, %: Cl 7.76; N 15.30.

3-(4-Nitro-2-furyl)-1-(4-tolyl)-2-propenone 2,4-dinitrophenylhydrazone (Vd). Yield 83%, mp 213–214°C (from AcOH). Found, %: N 15.98. $C_{20}H_{15}N_5O_7$. Calculated, %: N 16.02.

1-(4-Methoxyphenyl)-3-(4-nitro-2-furyl)-2-propenone 2,4-dinitrophenylhydrazone (Ve). Yield 84%, mp 208–209°C (from benzene). Found, %: N 15.39. $C_{20}H_{15}N_5O_8$. Calculated, %: N 15.45.

2-Nitro-3-(5-nitro-2-furyl)-1-phenyl-2-propenone 2,4-dinitrophenylhydrazone (Vf). Yield 82%, mp 257–258°C (from AcOH). Found, %: C 17.87. $C_{19}H_{12}N_6O_9$. Calculated, %: C 17.95.

1-Methyl-2-nitro-3-(5-nitro-2-furyl)-2-propenone 2,4-dinitrophenylhydrazone (Vg). Yield 80%, mp 255–256°C (from DMF). Found, %: N 20.63. $C_{14}H_{10}N_6O_9$. Calculated, %: N 20.69.

1-Methyl-3-(5-methyl-2-furyl)-2-nitro-2-propenone 2,4-dinitrophenylhydrazone (Vh). Yield 88%, mp 217–218°C (from dioxane). Found, %: N 18.75. $C_{15}H_{13}N_5O_7$. Calculated, %: N 18.67.

3-(4-Nitro-2-furyl)-2-propenal 2,4-dinitrophenylhydrazone (VI). Yield 68%, mp 245–246°C (from toluene). Found, %: N 20.51. $C_{13}H_9N_5O_7$. Calculated, %: N 20.17.

5-Acyl-4-furyl-1*H*-1,2,3-triazoles (VI). A mixture of 5 mmol of compound **III** and 5 mmol of sodium azide in 20 ml of DMF was stirred for 3 h at 60–70°C, cooled, diluted with water, and acidified to pH 1 with 10% hydrochloric acid. The precipitate was extracted into diethyl ether, the extract was evaporated, and the residue was recrystallized from glacial acetic acid.

5-Benzoyl-4-(5-nitro-2-furyl)-1*H*-1,2,3-triazole (VIf). Yield 59%, mp 184–185°C. Found, %: C 54.90; H 2.81; N 19.90. $C_{13}H_8N_4O_4$. Calculated, %: C 54.93; H 2.83; N 19.71.

5-Acetyl-4-(5-nitro-2-furyl)-1*H*-1,2,3-triazole (VIg). Yield 64%, mp 161–162°C. Found, %: C 43.23; H 3.06; N 25.02. $C_8H_6N_4O_4$. Calculated, %: C 43.25; H 2.72; N 25.21.

5-Acetyl-4-(5-methyl-2-furyl)-1*H*-1,2,3-triazole (VIh). Yield 82%, mp 162–163°C. Found, %: C 56.45; H 4.81; N 22.20. $C_9H_9N_3O_2$. Calculated, %: C 56.35; H 4.64; N 21.89.

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