BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 208—213 (1972)

Studies of the Synthesis of Furan Compounds. XXVI.[1] The Reaction of 5-Nitro-2-furimidoylhydrazine with Acid Anhydrides[2]

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(Received May 10, 1971)

Reactions between 5-nitro-2-furimidoylhydrazine (I) and acetic or propionic anhydride (or the corresponding acids) under various conditions afforded 5-methyl- (II) and 5-ethyl-2-(5-nitro-2-furyl)-1,3,4-oxadiazole (IV) and 5-methyl- (III), 5-ethyl- (IX), 1-acetyl-5-methyl- (VII), 1-propionyl-5-ethyl- (VIII), 1-propionyl-5-methyl- (X), and 1-acetyl-5-ethyl-3-(5-nitro-2-furyl)-1,2,4-triazole (XI) respectively. The treatment of I with acetic and propionic anhydride in refluxing benzene or tetrahydrofuran gave 1-acetyl- (V) and 1-propionyl-2-(5-nitro-2-furimidoyl)-hydrazine (VI) respectively. Compounds, VII, VIII, X, and XI were also prepared by the cyclization of V with propionic anhydride and by that of VI with acetic anhydride in dioxane. The structures of the products were discussed on the basis of the spectral data.

In continuation of our previous report on the preparation of several 5-nitro-2-furyl-heterocycles by the cyclization of 5-nitro-2-furimidoylhydrazine (I) with bifunctional compounds,[3] this paper will deal with the preparation of acyl (or without acyl)-(5-nitro-2-furyl)-5-alkyl-1,2,4-triazoles by the reaction of I with acid anhydries under various reaction conditions, and with the determination of the position of the acyl group in the triazole nucleus on the basis of the reactions of the acyl derivatives of I with acetic and propionic anhydrides.

Results and Discussion

Atkinson and Polya reported the synthesis of 1-methyl (or phenyl)-3-phenyl-1,2,4-triazole by the reaction of the corresponding 1-substituted 2-benzimidoylhydrazine with formic acid,[4] while Atkinson *et al.* reported that of 3-amino-5-alkyl (or aryl)-1,2,4-triazoles from an aminoguanidine salt and the appropriate organic acid in the presence of a small amount of nitric acid.[5] In a similar manner, when I was heated in glacial acetic acid, two products, II and III, were obtained. Compound II was identified as the 2-(5-nitro-2-furyl)-5-methyl-1,3,4-oxadiazole by an admixture-test and by a comparison of its IR spectrum with that of an authentic specimen,[3] while III was confirmed to be 3-(5-nitro-2-furyl)-5-methyl-1,2,4-triazole on the basis of the analytical and spectral data. The similar treatment of I with propionic acid afforded only one product, 2-(5-nitro-2-furyl)-5-ethyl-1,3,4-oxadiazole (IV) (Scheme 1).

1-Acetyl-(V) and 1-propionyl-2-(5-nitro-2-furimidoyl)-

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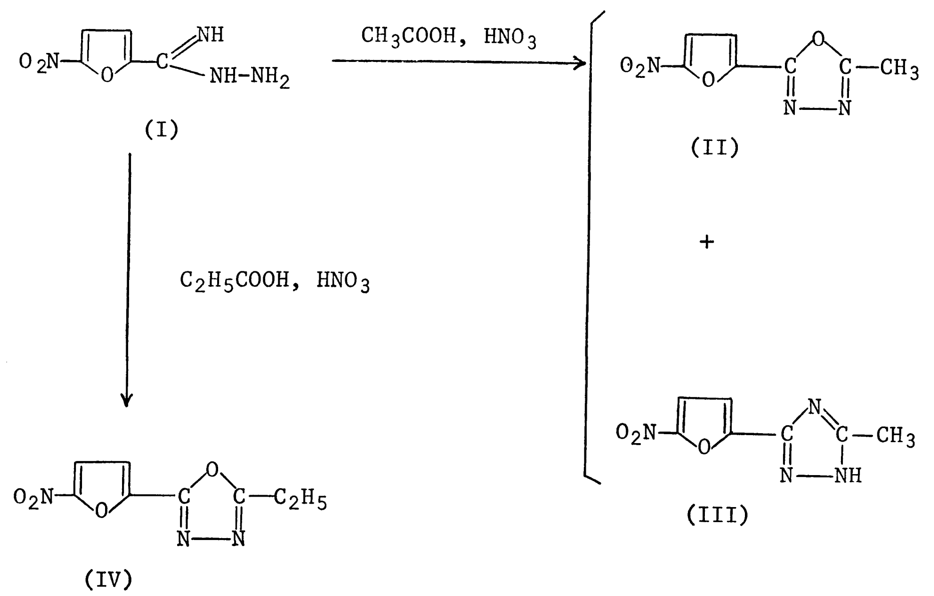
[1] Part XXV of this series; I. Hirao and Y. Kato, This Bulletin, **44**, 3136 (1971).

[2] Presented at the 24th Annual Meeting of the Chemical Soceity of Japan, Osaka, April, 1971.

[3] I. Hirao, Y. Kato, T. Hayakawa, and H. Tateishi, This Bulletin, **44**, 780 (1971).

[4] M. R. Atkinson and J. B. Polya, *J. Chem. Soc.*, **1953**, 1471; **1954**, 3319.

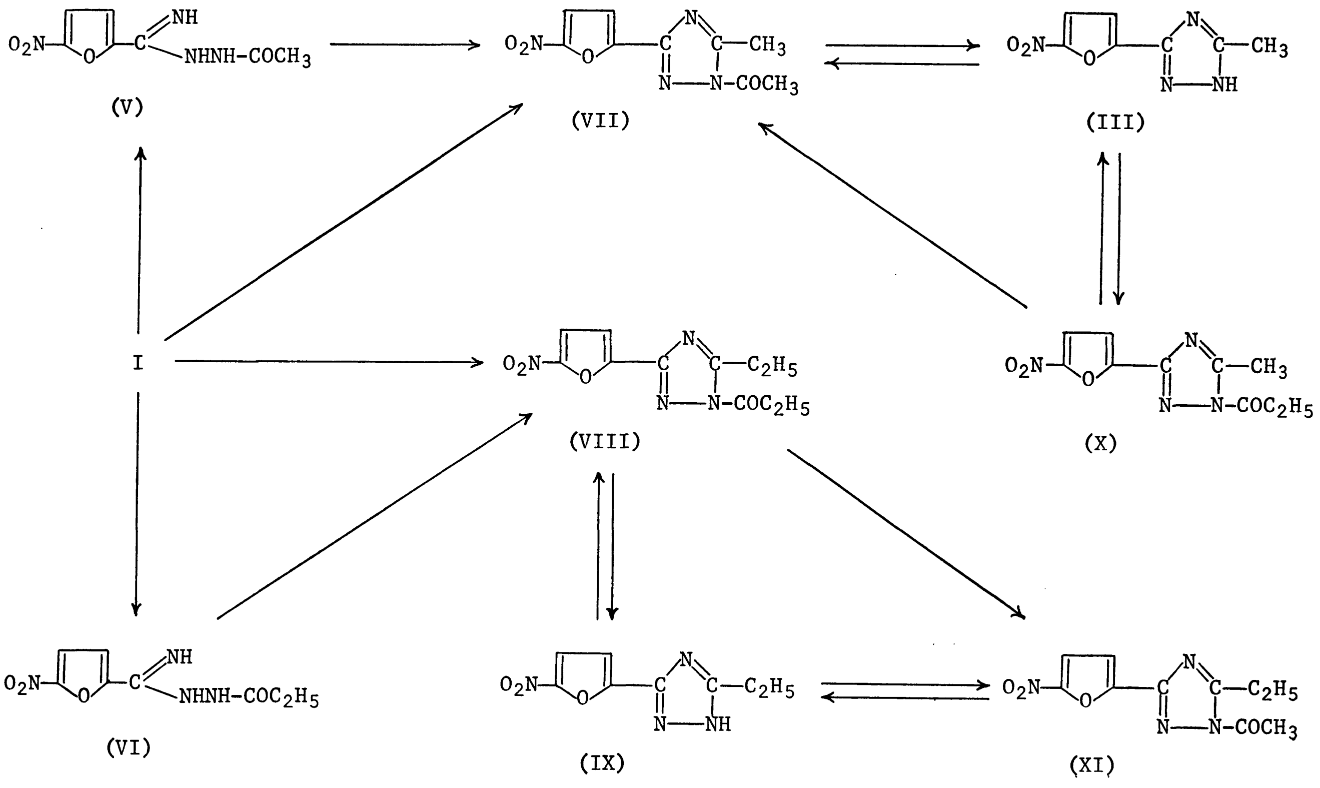
[5] M. R. Atkinson, A. A. Komzak, E. A. Parkes, and J. B. Polya, *ibid.*, **1954**, 4508.



Scheme 1

hydrazine (VI) were obtained by treating I with acetic and propionic anhydrides respectively in refluxing benzene or tetrahydrofuran. However, I afforded 1-acetyl-3-(5-nitro-2-furyl)-5-methyl-1,2,4-triazole (VII) and 1-propionyl-3-(5-nitro-2-furyl)-5-ethyl-1,2,4-triazole (VIII) when heated in large excesses of acetic and propionic anhydride respectively. Compounds VII and VIII were similarly obtained from, respectively, V and acetic anhydride, and VI and propionic anhydride.

When heated in water, VII afforded III, and VIII provided 3-(5-nitro-2-furyl)-5-ethyl-1,2,4-triazole (IX),



Scheme 2

Table 1. NMR data of III, VII, VIII, IX, X, and XI. (δ value, at 60 MHz)

	III	IX	VII	VIII	X		XI	
	in DMSO-d_6[a]				in DMSO-d_6	in CCl_3COOH[b]	in DMSO-d_6	in CCl_3COOH
Furan ring 4-H	7.76 (1H, d, J=4.0 Hz)	7.72 (1H, d, J=4.0 Hz)	7.71 (1H, d, J=4.0 Hz)	7.84 (1H, d, J=4.0 Hz)	7.81 (1H, d, J=4.0 Hz)	7.23[c] (2H, s)	7.81 (1H, d, J=4.0 Hz)	7.23[c] (2H, s)
Furan ring 3-H	7.19 (1H, d, J=4.0 Hz)	7.17 (1H, d, J=4.0 Hz)	7.35 (1H, d, J=4.0 Hz)	7.44 (1H, d, J=4.0 Hz)	7.42 (1H, d, J=4.0 Hz)		7.42 (1H, d, J=4.0 Hz)	
$\diagup\overset{\|}{\mathrm{C}}\mathrm{-CH_3}$	2.46 (3H, s)		2.74[d] (6H, s)		2.74 (3H, s)	2.62 (3H, s)		
$\mathrm{-CO-CH_3}$							2.74 (3H, s)	1.86 (3H, s)
$\diagup\overset{\|}{\mathrm{C}}\mathrm{-CH_2-}\underset{\mid}{\overset{\mid}{\mathrm{C}}}\mathrm{-}$		2.80 (2H, q, J=7.5 Hz)		3.19 (2H, q, J=7.5 Hz)			3.15 (2H, q, J=7.5 Hz)	2.94 (2H, q, J=7.5 Hz)
$\diagup\overset{\|}{\mathrm{C}}\mathrm{-}\underset{\mid}{\overset{\mid}{\mathrm{C}}}\mathrm{-CH_3}$		1.30 (3H, t, J=7.5 Hz)		1.37 (3H, t, J=7.5 Hz)			1.33 (3H, t, J=7.5 Hz)	1.16 (3H, t, J=7.5 Hz)
$\mathrm{-CO-CH_2-}\underset{\mid}{\overset{\mid}{\mathrm{C}}}\mathrm{-}$				3.22 (2H, q, J=7.5 Hz)	3.18 (2H, q, J=7.5 Hz)	2.14 (2H, q, J=7.5 Hz)		
$\mathrm{-CO-}\underset{\mid}{\overset{\mid}{\mathrm{C}}}\mathrm{-CH_3}$				1.23 (3H, t, J=7.5 Hz)	1.19 (3H, t, J=7.5 Hz)	0.82 (3H, t, J=7.5 Hz)		

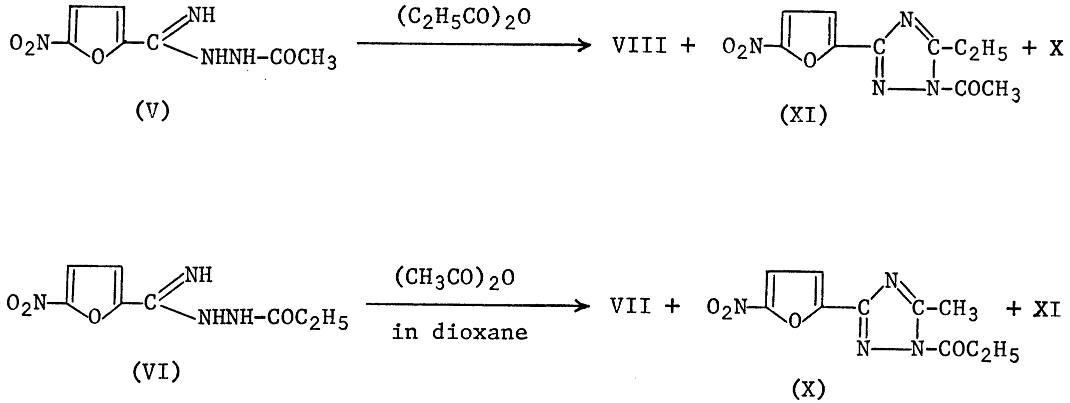
a) TMS was used as the internal standard. b) HMDS was used as the internal standard. c) Two protons of the furan ring were overlapped and showed a singlet. d) The CH_3 and $COCH_3$ protons appeared the same field and formed a singlet.

both in almost quantitative yields. III was reverted to VII by heating it in acetic anhydride, and IX, to VIII in propionic anhydride. 1-Propionyl-5-methyl- (X) and 1-acetyl-5-ethyl-3-(5-nitro-2-furyl)-1,2,4-triazole (XI) were obtained by the treatment of III with hot propionic anhydride, and by the treatment of IX with hot acetic anhydride, whereas X and XI reverted to III and IX respectively upon heating with water. Furthermore, X was converted into VII, and also VIII into XI, by heating them with acetic anhydride. These results show that the acyl group on a nitrogen of the triazole nucleus could be replaced easily be an acyl group of the acid anhydride employed (Scheme 2).

The IR spectra showed a characteristic wide ammonium absorption in the 3010—2550 cm^{-1} region for III, and in the 3150—2800 cm^{-1} region for IX. This fact, as has been discussed previously,[3] suggests that both III and IX contribute to an intermolecular association because of the hydrogen transfer between two adjacent molecules. Neither the spectrum of III nor that of IX showed the C=O stretching absorption which was observed at 1680 cm^{-1} in the spectra of compounds V and VI. In the finger-print region, III had a sharp band at 1058 cm^{-1} due to a methyl rocking vibration, and IX contained three absorptions, at 1062, 1048, and 842 cm^{-1}. The 1048 cm^{-1} band is assigned to the CH_3 rocking vibration, and the 1062 and 842 cm^{-1} bands to the C–H wagging motion of the $-C_2H_5$ group.

On comparing the IR spectra of the four acyl compounds (VII, VIII, X, and XI), all of them were found to show a strong absorption band, VII at 1756, VIII at 1738, X at 1759, and XI at 1754 cm^{-1} due to the C=O stretching vibration. The weak to medium bands due to the C–H stretching motion in VII, VIII, X, and XI appeared in the 3000—2800 cm^{-1} region. In the finger-print regions, the band assignable to the CH_3 rocking mode in VII was observed at 1091 cm^{-1} and also in X at 1089 cm^{-1}. In the compound VIII, the 1084, 1060, and 828 cm^{-1} bands, and in XI, the 1085, 1060, and 830 cm^{-1}, bands might be assignable much as in the mother compound, IX. Two strong bands and a weak one appeared at 962, 646, and 727 cm^{-1} respectively in VII; the corresponding ones at 962, 646, and 723 cm^{-1} in XI were assigned to a $-COCH_3$ group introduced, while the bands due to the $-COC_2H_5$ motion in VIII are observed as a weak band at 964 cm^{-1} and a strong one at 943 cm^{-1}, while those in X are observed at 965 and 943 cm^{-1}.

The NMR spectra in DMSO-d_6 supported the structures of III, VII, VIII, IX, X, and XI presented above. As is shown in Table 1, the chemical shifts of the ring methyl or methylene protons of VII, VIII, X, and XI shifted to a lower magnetic field than those of III or IX upon the introduction of an acetyl or propionyl group. This indicates that the acyl group may be introduced into the vicinal nitrogen atom next to the existing alkyl group. The NMR spectra of X and XI in DMSO-d_6 were different from those in trichloroacetic acid (Table 1). Both the acetyl protons and the methylene protons of a propionyl group are more subject to the solvent effect than are the methyl and methylene protons attached to the triazole ring, and their chemical shifts shifted to a higher magnetic field. The C_4-proton of the furan nucleus was very subject to the solvent effect and revealed the signal together, with that of the C_3-ptoton



Scheme 3

at 7.23 ppm of hexamethyldisiloxane (HMDS); accordingly, the signals were observed as a singlet.

On the treatment of VI with a large excess of acetic anhydride in dioxane at 95—100°C for 1 hr, a mixed product was obtained. The components were successfully resolved by treating the mixture with hot ligroin. The ligroin-insoluble part was confirmed to be VII on the basis of the analytical and spectral data. From the ligroin solution, a crystalline powder (XII) (mp 103—105°C) was obtained. The results of an elemental analysis of XII was in good accordance with the calculated value for $C_{10}H_{10}N_4O_4$ (X or XI). Subsequent crystallization from ligroin raised the melting point to 112—114°C, but the results of the elemental analysis were unchanged. In addition, the IR spectrum of XII did not agree with that of X or XI, and it had bands at 980, 955, 725, and 645 cm^{-1}, indicating the presence of both acetyl and propionyl groups. The NMR spectrum as is shown in Fig. 1a, revealed signals at (δ from TMS in DMSO-d_6) 1.26 (q, J=7.5 Hz), 2.74 (s), *ca.* 2.95—3.35 (m), 7.42 (d, J=4.0 Hz), and 7.80 (d, J=4.0 Hz), with relative intensities of 3:3:2:1:1. However, when measured in trichloroacetic acid, the NMR spectrum (Fig. 2b) varied remarkably and showed signals at (δ from HMDS) 0.82 (t, J=7.5 Hz), 1.16 (t, J=7.5 Hz), 1.86 (s), 2.15 (q, J=7.5 Hz), 2.62 (s), 2.94 (q, J=7.5 Hz) and 7.23 (s) (the signal intensity ratio; 0.58: 0.93: 0.92: 0.40: 0.58: 0.62: 1). Considering these data, it was concluded that XII was obviously a mixture of X and XI, and that the component ratio (X:XI) was 39:61 (on the basis of the NMR intensity ratio).

The similar treatment of V with propionic anhydride also produced three compounds, VIII, X, and XI, in the proportion of 1: 0.8: 0.6.

A modern representation of the structure of 1,2,4-triazole takes cognizance of the imino hydrogen atom not being attached to any of the nitrogen atoms, but rather existing as a charged atom closely bound by a negatively-charged triazole nucleus stabilized by resonance.⁶⁾ The substitution reaction upon the imino nitrogen of triazole could, then, give three isomeric *N*-substituted derivatives (1-, 2-, and 4-substituted derivatives). In this investigation, none of the isomeric acetyl or propionyl derivatives were isolated, but only a sort of product was obtained in each type of derivative. It is very difficult to determine the position of an acyl group substituted on the triazole nucleus, fortunately, however, we could confirm the formation of XI from the reaction of V with propionic anhydride and from that of X from VI and acetic anhydride by studying the NMR spectra. Consequently, it seems reasonable to conclude that the position of the introduced acyl group of VII, VIII, X, and XI is the vicinal nitrogen atom, far from the 5-nitro-2-furyl group, as has been discussed above.

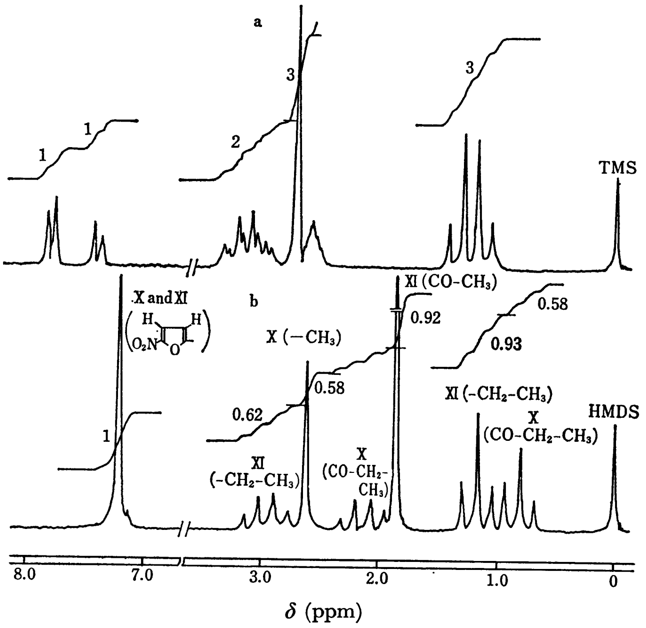


Fig. 1. NMR spectra of XII (mixture of X and XI).
a: measured in DMSO-d_6 at 24°C
b: measured in CCl_3COOH at 70°C

Experimental

All the melting and decomposition points are uncorrected. The elemental analyses were performed on a Yanagimoto C. H. N. Corder, MT-2 type. The infrared absorption spectra (IR) were measured in potassium bromide discs on a Hitachi grating infrared spectrophotometer, Model EPI-G3.

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6) K. T. Potts, *Chem. Rev.*, **61**, 87 (1961). The π-electron densities for 1,2,4-triazole were published in the following literature: a) L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951). b) M. R. Atkinson and J. B. Polya, *J. Chem. Soc.*, **1954**, 3319. c) S. Basu, *Proc. Natl. Inst. Sci. India*, **21A**, 173 (1955).

The nuclear magnetic resonance spectra (NMR) were determined by means of a Nihon-Denshi NMR spectrometer, JNM C-60HL (60 MHz). The spectra were measured in DMSO-d_6 at 24°C with tetramethylsilane (TMS) as the internal standard, and in trichloroacetic acid at 70°C with hexamethyldisiloxane (HMDS) as the internal standard; the chemical shifts are expressed in δ-values.

2-(5-Nitro-2-furyl)-5-methyl-1,3,4-oxadiazole (II) and 3-(5-Nitro-2-furyl)-5-methyl-1,2,4-triazole (III). 5-Nitro-2-furimidoylhydrazine[7] (I) (3 g, 17.6 mmol), glacial acetic acid (50 m*l*), and nitric acid (5 drops) were heated under reflux for 2 hr. After cooling, water (100 m*l*) was added and the mixture was extracted with ether (500 m*l*). The ether extracts were washed with water and dried over anhydrous sodium sulfate. After the concentration of the extracts, the residue was treated with hot benzene (50 m*l*) and the insoluble product was filtered off while hot. Thus, the crude material of III was obtained as an ochreous powder; mp 232—234°C; 0.7 g. Recrystallization from water gave yellow needles; mp 243—244°C. The yield was 0.6 g (17.5%).

Found: C, 43.05; H, 2.95; N, 28.55%. Calcd for $C_7H_6N_4O_3$ (III): C, 43.29; H, 3.09; N, 28.86%.

On cooling of the benzene filtrate, a yellow-ochre powder (0.5 g) was obtained; mp 138—148°C. Crystallization from ethanol afforded pale yellow needles; mp 153—154°C. Yield, 0.3 g (8.7%).

Found: C, 43.54; H, 2.35; N, 21.92%. Calcd for $C_7H_5N_3O_4$ (II): C, 43.07; H, 2.56; N, 21.53%.

This product was identified as the 1,3,4-oxadiazole (II) by an admixture-test and by a comparison of the IR spectrum with that of an authentic specimen.[3]

2-(5-Nitro-2-furyl)-5-ethyl-1,3,4-oxadiazole (IV). A mixture of I (1 g, 5.8 mmol), propionic acid (20 m*l*), and nitric acid (3 drops) was refluxed for 2 hr. Work-up as above afforded 0.3 g (24.4%) of IV, mp 182—183°C, as yellow needles (recrystallized from benzene-ligroin).

Found: C, 46.30; H, 3.36; N, 20.20%. Calcd for $C_8H_7N_3O_4$: C, 45.93; H, 3.35; N, 20.10%.

1-Acetyl- (V) or 1-Propionyl-2-(5-nitro-2-furimidoyl)hydrazine (VI). Acetic or propionic anhydride (each 20 mmol) was added slowly to a stirred solution of I (3.4 g, 20 mmol) in 100 m*l* of benzene (or 70 m*l* of tetrahydrofuran). The mixture was then stirred vigorously at room temperature for 1 hr. After cooling, the product was filtered and recrystallized from methanol. V; orange-yellow cylinders; mp 211—212°C decomp. Yield, 3.96 g (93.3%).

Found: C, 39.98; H, 3.73; N, 26.74%. Calcd for $C_7H_8N_4O_4$ (V): C, 39.62; H, 3.77; N, 26.42%.

VI; orange-yellow needles; mp 216—217°C decomp. Yield, 4.18 g (92.5%).

Found: C, 42.82; H, 4.48; N, 24.77%. Calcd for $C_8H_{10}N_4O_4$ (VI): C, 42.47; H, 4.42; N, 24.78%.

If the recrystallization was achieved from water, V was obtained as its semi-hydrate of yellow needles; mp 210°C.

Found: C, 38.52; H, 4.11; N, 25.31%. Calcd for $C_7H_8N_4O_4 \cdot \frac{1}{2}H_2O$: C, 38.01; H, 4.07; N, 25.34%.

1-Acetyl-3-(5-nitro-2-furyl)-5-methyl-1,2,4-triazole (VII).
From I and Acetic Anhydride: A solution of I (3.4 g, 20 mmol) in 50 m*l* of acetic anhydride was stirred at room temperature for 1 hr and then heated under reflux for an additional hour. On cooling, the separated product was collected and washed with benzene to afford 3.4 g (72%) of VII (mp 210—213°C) as pale yellow needles. Recrystallization from acetone gave pale yellow needles; mp 211—212°C.

Found: C, 45.73; H, 3.39; N, 23.72%. Calcd for $C_9H_8N_4O_4$: C, 45.76; H, 3.39; N, 23.73%.

From V and Acetic Anhydride: A mixture of V (2.12 g, 10 mmol) and acetic anhydride (30 m*l*) was refluxed for 1 hr. Subsequent work-up as above afforded 1.85 g (78.4%) of pale yellow needles. Mp 211—212°C; undepressed upon admixture with a sample prepared by the above method.

From the Acetylation of III: Compound III (1.94 g, 10 mmol) was covered with acetic anhydride (20 m*l*) and heated under reflux for 1 hr. The excess acid anhydride was then removed *in vacuo*, and the residue was recrystallized from acetone to give 1.9 g (80%) of VII as pale yellow needles, mp 210—211°C. This product was found to be identical with VII by a mixed-melting-point determination and by a comparison of the IR spectrum with that of an authentic sample.

1-Propionyl-3-(5-nitro-2-furyl)-5-ethyl-1,2,4-triazole (VIII).
From I and Propionic Anhydride: This was prepared in the same way as was VII, but using propionic anhydride (50 m*l*). The resulting solution was taken to dryness *in vacuo*, and the residue was crystallized from ligroin to give 2.9 g (55%) of VIII as pale brown granules; mp 78—79°C.

Found: C, 49.75; H, 4.48; N, 20.92%. Calcd for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.54; N, 21.21%.

From VI and Propionic Anhydride: VI (2.26 g, 10 mmol) and propionic anhydride (20 m*l*) were heated together under reflux for 1 hr. The excess acid anhydride was removed *in vacuo*, and the oily residue was solidified by cooling, washed with ether, and then dried. Thus, 1.8 g of the crude product were obtained; mp 69—72°C. Subsequent recrystallization from ligroin gave 1.46 g (55.3%) of pale yellow granules; mp 78—79°C. This product was found to be identical with VIII by a mixed-melting-point determination.

From the Acylation of IX with Propionic Anhydride: The procedure outlined above for VII was followed using IX (2.08 g, 10 mmol) and propionic anhydride (20 m*l*). A work-up as above afforded 1.85 g (70%) of pale brown granules melting at 80—81°C. The product was shown to be the same as above by a study of its IR spectrum and by its failure to depress the melting point when mixed with a sample prepared by the above method.

1-Propionyl-3-(5-nitro-2-furyl)-5-methyl-1,2,4-triazole (X). The procedure outlined above for VII was employed using III (0.97 g, 5 mmol) and propionic anhydride (25 m*l*). Work-up as above gave 1.03 g (82.3%) of pale yellow cylinders; mp 148—149°C (from ligroin).

Found: C, 48.12; H, 4.08; N, 22.62%. Calcd for $C_{10}H_{10}N_4O_4$: C, 48.00; H, 4.00; N, 22.40%.

1-Acetyl-3-(5-nitro-2-furyl)-5-ethyl-1,2,4-triazole (XI). The procedure outlined above for VII was followed using IX (1.04 g, 5 mmol) and acetic anhydride (40 m*l*). A work-up as above then afforded 1.09 g (87.6%) of XI as pale yellow needles which melted at 119°C.

Found: C, 48.11; H, 4.11; N, 22.29%. Calcd for $C_{10}H_{10}N_4O_4$: C, 48.00; H, 4.00; N, 22.40%.

Hydrolyses of VII, VIII, X, and XI. Five mmol of acyl-triazole (VII, VIII, X, or XI) were heated in 100 m*l* of water under reflux for 1 hr. On cooling, the hydrolyzed product (III or IX) was separated as pale yellow needles; the needles were filtered, washed with a small amount of cold water, and then dried. The yield were almost quantitative. Recrystallization was achieved from water when the purity was unsatisfactory. IX; pale yellow needles; mp 179—181°C.

Found: C, 46.45; H, 3.80; N, 26.67%. Calcd for $C_8H_8N_4O_3$ (IX): C, 46.15; H, 3.85; N, 26.95%.

Reaction of VIII or X with Acetic Anhydride. Acetic anhydride (30 m*l*) and the propionyl-triazole VIII (or X)

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[7] Y. Kato and I. Hirao, *Bull. Kyushu Inst. Technol.*, No. 15, 57 (1965).

(5 mmol) were heated together under reflux for 1 hr. On cooling or concentration, a crude product was obtained; it was then recrystallized from ligroin (acetone) to afford pure XI (or VII) in a 66% (69%) yield.

Reaction of VI with Acetic Anhydride in Dioxane. A mixture of VI (2.26 g, 10 mmol), acetic anhydride (10.2 g, 0.1 mol), and dioxane (50 m*l*) was heated at 100°C for 1 hr. The solvent and acid anhydride were removed *in vacuo*, and the residue was heated in ligroin (100 m*l*) under reflux. The insoluble material was filtered while hot and recrystallized from acetone to afford VII as pale yellow needles, which melted at 211—212°C and which weighed 0.4 g (17%). This was identical in its IR spectrum with an authentic sample of VII.

On the concentration of the mother filtrate, a light yellow, crystalline product was obtained. Mp 103—105°C; the yield was 1.35 g.

Found: C, 48.34; H, 3.71; N, 22.73%. Calcd for $C_{10}H_{10}N_4O_4$ (X and XI): C, 48.00; H, 4.00; N, 22.40%.

Recrystallization from ligroin raised the melting point to 112—114°C, but the value of the elemental analysis was unchanged. This product was identified as a mixture of X and XI by a study of its IR and NMR spectra. However, the resolution of X and XI could not be achieved by solvents or solvent pairs. The compound ratio (X: XI) was determined to be 39: 61 on the basis of the NMR intensity ratio of the methyl and acetyl proton (in CCl_3COOH).

Reaction of V with Propionic Anhydride. A mixture of V (2.12 g, 10 mmol) and propionic anhydride (20 m*l*) was heated under reflux for 1 hr. A work-up as above afforded 0.65 g of pale yellow crystals (mp 108—110°C) as the first precipitate from the ligroin solution.

Found: C, 48.36; H, 4.12; N, 22.41%. Calcd for $C_{10}H_{10}N_4O_4$ (X and XI): C, 48.00; H, 4.00; N, 22.40%.

This substance was confirmed to be a mixture of X and XI on the basis of its IR and NMR spectra. The compound ratio was determined to be X: XI=8: 5 by the NMR method, using trichloroacetic acid as the solvent.

The ligroin filtrate was concentrated *in vacuo*, and the residue was crystallized from petroleum ether to give 0.53 g (20%) of VIII as pale yellow granules; mp 79—80°C. The melting point of this compound was not depressed upon admixture with an authentic sample of VIII.

The authors are indebted to Mr. T. Hayakawa and Mr. T. Shiraishi for their help in the experimental work.