Studies on Furan Derivatives. II. (1)
Preparation of α-Substituted β-2-(5-Nitrofuryl)vinylamines

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α-Substituted β-2-(5-nitrofuryl)vinylamines were synthesized from α-aryl-β-2-(5-nitrofuryl)-acryloyl azides and *N*-[α-substituted β-2-(5-nitrofuryl)vinyl]pyridinium bromides.

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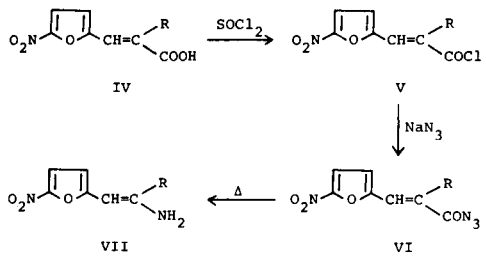
In a previous paper (2), we reported that thermolysis of α-2-furyl-β-2-(5-nitrofuryl)acryloyl azide (I) in dried dioxane gave α-2-furyl-β-2-(5-nitrofuryl)vinylisocyanate (II) which easily underwent hydrolysis to give an interesting primary vinylamine, namely α-2-furyl-β-2-(5-nitrofuryl)-vinylamine (III). Thermolysis of I in dioxane containing a small amount of water gave III directly as a main product. Primary vinylamines are usually unstable and susceptible to hydrolysis giving ketones. Accordingly, they have not been widely used as synthetic materials. H. Ahlbrecht (3) has reported that when primary vinylamines are conjugated with an electron-withdrawing group, such as a nitrophenyl group, they become appreciable stable. Thus, β-2-(5-nitrofuryl)vinylamines aroused the authors' interest as a model for studying the reactions of primary vinylamines, since these compounds are primary vinylamines conjugated with a strong electron-withdrawing 5-nitro-2-furyl group. Only one nitrofuran vinylamine derivative, β-2-(5-nitrofuryl)-β-carbamoylvinylamine is known (4). Thus, the authors attempted to prepare a new class of compounds, α-substituted β-2-(5-nitrofuryl)vinylamines, from α-aryl-β-2-(5-nitrofuryl)acryloyl azides or *N*-[α-substituted β-2-(5-nitrofuryl)vinyl]pyridinium bromides.

It is well known that the Curtius rearrangement of acylazides to isocyanates, followed by hydrolysis gives primary amines. However the preparation of primary vinylamines from vinylacylazides or vinylisocyanates has not been reported. Consequently, the thermolysis of α-aryl-β-2-(5-nitrofuryl)acryloyl azides (VIa-g) in aqueous media was carried out in order to prepare some β-2-(5-nitrofuryl)vinylamines. First, α-aryl-β-2-(5-nitrofuryl)acrylic acids (IVa-g) were converted to the corresponding acid chlorides (Va-g) with thionyl chloride. Compounds Va-g were reacted with sodium azide to give α-aryl-β-2-(5-nitrofuryl)acryloyl azides (VIa-g), which could not be purified, being very unstable towards light and heat. The ir spectra of VIa-g all showed an absorption band at around 2150 cm^{-1} attributed to $-N_3$. α-Aryl-β-2-(5-nitrofuryl)vinylamines (VIIa-g) were formed in good yields by refluxing VIa-g in water-dioxane (1:9) or water-benzene (1:1); the end of the reaction could be recognized by a cease of evolution of nitrogen and carbon dioxide gasses

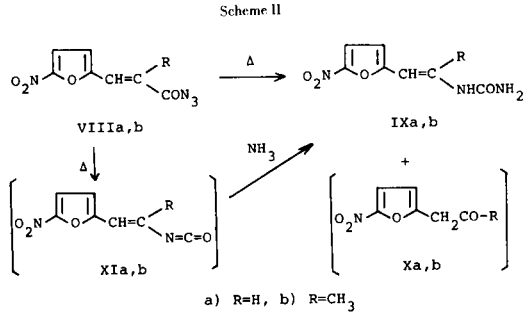
Scheme I



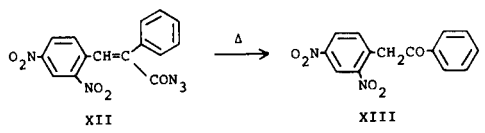
(1-2 hours). The structures of VIIa-g were confirmed by the results of various spectral data and elemental analyses.

However thermolysis of β-2-(5-ntirofuryl)acryloyl azide (VIIIa) in water-dioxane gave only β-2-(5-nitrofuryl)vinylurea (IXa) instead of the expected primary vinylamine. Compound IXa was identified on the basis of elemental analysis and some spectral data. Compound IXa was also prepared by the reaction of β-2-(5-nitrofuryl)vinylisocyanate (XIa) with ammonia. Similarly, the thermolysis of α-methyl-β-2-(5-nitrofuryl)acryloyl azide (VIIIb) gave only α-methyl-β-2-(5-nitrofuryl)vinylurea (IXb). With respect to the pathway for the formation of IXa and b, it could be expected that first the corresponding isocyanates (XIa, b) were produced, followed by part of the isocyanates being hydrolyzed to give ketones (Xa,b) and ammonia, and then the unreacted isocyanates reacting with ammonia to give IXa,b. However, Xa,b could not be isolated, for

Scheme II



Scheme III



they are unstable under such reaction conditions. In addition, thermolysis of α-phenyl-β-2,4-dinitrophenylacryloyl azide (XII), which possesses a strong electron-withdrawing group at the β-position was carried out in order to study the behavior of this reaction toward the benzene system, but the sole product was 2,4-dinitrophenylmethyl phenyl ketone (XIII).

Since the limitations were recognized in preparing primary vinylamines from β-2-(5-nitrofuryl)acryloyl azides, an alternative method was studied. Krönhke, *et al.*, (5) have reported the preparation of primary stilbylamines from *N*-stilbylpyridinium halides. The application of Krönhke's method was examined with respect to nitrofuran derivatives. *N*-[α-Ethoxycarbonyl-, α-benzoyl- or α-2-(5-nitrofuryl)-β-2-(5-nitrofuryl)vinyl]pyridinium bromides (XIVa-c) were prepared by the condensation of 5-nitro-2-furfural with *N*-substituted pyridinium bromides. When excess morpholine or piperidine was added to a solution of XIVa-c in ethanol under stirring at 0°, α-ethoxycarbonyl-, α-benzoyl- or α-2-(5-nitrofuryl)-β-2-(5-nitrofuryl)vinylamines (XVa-c) were obtained in 10-40% yields. These low yields may be due to the fact that the nitrofuran ring is unstable under basic condition. The structures of XVa-c were confirmed by the results of various spectral data and elemental analyses.

The ir spectra of VIIa-g and XVa-c showed two absorption bands in the 3300-3350 cm^{-1} region, indicating $-NH_2$. In their nmr spectra, vinylene (1H) and amine (2H) signals could be obviously perceived. Ahlbrecht (3) has observed that the stilbylamines exhibit imine-enamine equilibria in their nmr spectra. However, the nmr spectra (in DMSO-d_6) of VIIf and III showed only a pattern of the corres-

Scheme IV

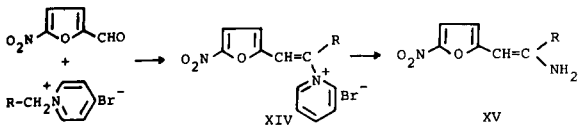


Table I

α-Substituted β-2-(5-Nitrofuryl)vinylamines

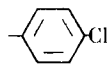
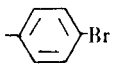
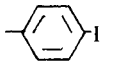
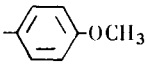
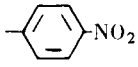
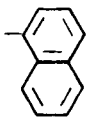
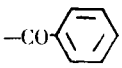
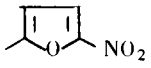
Compound No.	R	Yield (%)	M.p. (°C)	Formula	Analyses Calcd. (Found)		
VIIa		65	119-121	$C_{12}H_{10}N_2O_3$	62.60 (62.79)	4.38 (4.21)	12.17 (12.00)
VIIb		76	155-157	$C_{12}H_9ClN_2O_3$	54.45 (54.38)	3.43 (3.30)	10.59 (10.34)
VIIc		63	173-174	$C_{12}H_9BrN_2O_3$	46.62 (46.26)	2.93 (2.91)	9.06 (8.95)
VIId		65	189-191	$C_{12}H_9IN_2O_3$	40.47 (40.76)	2.55 (2.49)	7.87 (8.19)
VIIe		25	178-179	$C_{13}H_{12}N_2O_4$	59.99 (60.23)	4.65 (4.66)	10.77 (10.77)
VIIf		95	177-178	$C_{12}H_9N_3O_5$	52.37 (52.70)	3.30 (3.31)	15.27 (15.56)
VIIg		30	148-150	$C_{16}H_{12}N_2O_3$	68.56 (68.24)	4.32 (4.18)	10.00 (9.72)
XVa	—COOEt	40	104-105	$C_9H_{10}N_2O_5$	47.79 (48.05)	4.46 (4.28)	12.39 (12.20)
XVb		10	93-94	$C_{10}H_7N_3O_6$	60.46 (60.30)	3.90 (3.80)	10.85 (10.59)
XVc		23	218-220	$C_{10}H_7N_3O_6$	45.29 (45.60)	2.66 (2.38)	15.85 (15.50)

Table II

Nmr (a) δ (Acetone-d_6) of α-Substituted β-2-(5-Nitrofuryl)vinylamines

Compound No.	-CH=	NF (b) -3H	NF (b) -4H	Aromatic-H	NH_2	$-CH_2-$, $-CH_3$
VIIa	5.60 (s)	6.52 (d, J = 4)	7.40-8.00 (6H, m)		6.00-7.00 (b)	-----
VIIb	6.68 (s)	6.63 (d, J = 4)	7.74 (d, J = 4)	7.69 (2H, d, J = 9) 7.89 (2H, d, J = 9)	6.00-7.00 (b)	-----
VIIc	5.66 (s)	6.62 (d, J = 4)	7.72 (d, J = 4)	7.83 (4H, s)	6.20-6.90 (b)	-----
VIId	5.67 (s)	6.58 (d, J = 4)	7.73 (d, J = 4)	7.68 (2H, d, J = 9) 7.97 (2H, d, J = 9)	6.00-7.00 (b)	-----
VIIe	5.62 (s)	6.56 (d, J = 4)	7.73 (d, J = 4)	7.20 (2H, d, J = 9) 7.83 (2H, d, J = 9)	6.10-6.90 (b)	3.93 (3H, s)
VIIf	5.83 (s)	6.62 (d, J = 4)	7.74 (d, J = 4)	8.18 (2H, d, J = 9) 8.47 (2H, d, J = 9)	6.20-7.00 (b)	-----
VIIg	5.35 (s)	6.51 (d, J = 4)	7.50-8.50 (8H, m)		6.20-7.10 (b)	-----
XVa	6.27 (s)	6.83 (d, J = 4)	7.70 (d, J = 4)	-----	5.70-6.50 (b)	1.37 (3H, t, J = 7) 4.39 (2H, q, J = 7)
XVb	5.86 (s)	6.88 (d, J = 4)	7.60-8.00 (6H, m)		5.70-6.50 (b)	-----
XVc	6.08 (s)	6.71 (d, J = 4) 7.31 (d, J = 4)	7.61 (d, J = 4) 7.64 (d, J = 4)	-----	5.70-6.70 (b)	-----

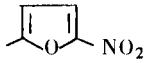
(a) s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. (b) NF =  NO_2

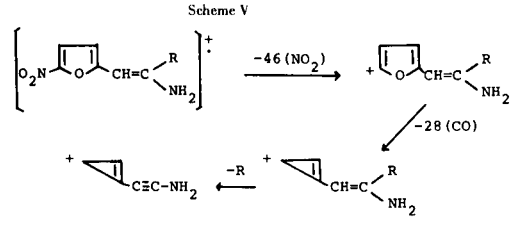
Table III

α-Substituted β-2-(5-Nitrofuryl)vinylamines

Compound No.	Ir ν max (nujol) cm^{-1} for NH_2	Uv λ max (ethanol) nm (log ε)	Ms m/e (M^+)
VIIa	3390, 3500	265 (4.15), 488 (4.36)	230
VIIb	3380, 3480	265 (4.10), 485 (4.31)	264
VIIc	3370, 3480	263 (4.13), 484 (4.34)	308
VIId	3370, 3480	263 (4.17), 487 (4.37)	356
VIIe	3360, 3490	275 (4.12), 503 (4.42)	260
VIIf	3390, 3500	270 (4.36), 480 (4.37)	275
VIIg	3310, 3480	265 (4.34), 480 (4.37)	280
XVa	3370, 3500	278 (4.03), 440 (4.19)	226
XVb	3370, 3500	259 (4.09), 449 (4.29)	258
XVc	3340, 3460	284 (4.18), 485 (4.38)	265

ponding enamine form at room temperature, 80° and 120°, respectively. The uv absorption maxima of VIIa-g and XVc shifted to longer wavelength regions in comparison with the corresponding β-2-(5-nitrofuryl)vinyls (6) and α,β-di-*p*-nitrophenylvinylamine (7). These data suggest that the β-nitrofuran ring is strongly conjugated with the vinylamine system. In their mass spectra, a common

Scheme V



cleaving pattern was observed. That is, all these compounds characteristically showed that the nitro group left first, followed by the CO fragment of the furan ring. The peaks with respect to the cleavage of α-substituents were also observed significantly. Such cleaving pattern was supported by the existence of methastable ions.

In the thermolysis of some acryloyl azides in aqueous media: β-2-(5-nitrofuryl)acryloyl azides (IVa-g) possessing an α-aryl group gave mainly primary vinylamines (VIIa-g). β-2-(5-nitrofuryl)acryloyl azides possessing an α-hydrogen or an α-methyl group gave ureas (IXa,b) and α-phenyl-β-2,4-dinitrophenylacryloyl azide possessing a β-phenyl group instead of a 5-nitro-2-furyl group gave only the ketone (XIII). Thus an aromatic group such as aryl or heteroaryl (2) groups would be necessary at the α-position in order to isolate β-2-(5-nitrofuryl)vinylamines as stable compounds.

The derivatives mentioned above were subjected to antibacterial activity tests, exhibiting little biological activity with the exception of VIIb, VIIe and VIIg, which showed activity against *B. Subtilus* (minimum inhibitory concentration 3.13-12.5 μg./ml.).

EXPERIMENTAL

All melting points are uncorrected. The nmr spectra were obtained with JEOL JNM-60HL and JEOL PS-100 spectrometers and the chemical shift in ppm was determined using tetramethylsilane as an internal standard; ir spectra were taken on a JASCO IRI-1; mass spectra were measured (direct solid inlet) by a SHIMAZU LKB-9000; uv spectra were recorded by a JASCO UVIDEC-1.

α-Phenyl-β-2-(5-nitrofuryl)vinylamine (VIIa).

A mixture of 5 g. (0.019 mole) of IVa, 4.6 g. (0.045 mole) of thionyl chloride and 30 ml. of dried benzene was refluxed for 4 hours and the solvent was removed *in vacuo*. The oily residue (Va) was dissolved in 20 ml. of acetone. The acetone solution of Va was added portionwise to a stirred solution of 1.9 g. (0.029 mole) of sodium azide in 20 ml. of water at 10-20°. Stirring was continued for 20 minutes after the addition was complete, then 100 ml. of water was added and the mixture was stirred for an additional 30 minutes. The produced yellow crystals (VIa) were then filtered, m.p. 67-70° dec.; ir ν max (nujol) cm^{-1}: 2130 (N_3), 1665 (C=O). Compound VIa was refluxed for 20 minutes in water (10 ml.)-dioxane (90 ml.) and then poured into ice water and filtered. The red precipitate was recrystallized from methanol to give red needles (VIIa), 3 g., m.p. 124-125°.

α-4-Chlorophenyl-β-2-(5-nitrofuryl)vinylamine (VIIb).

A mixture of 9.5 g. (0.032 mole) of IVb, 5.8 g. (0.49 mole) of thionyl chloride and 70 ml. of benzene was refluxed for 1.5 hours and the solvent was removed *in vacuo*. The oily residue (Vb) was dissolved in 100 ml. of acetone. A solution of Vb was added portionwise to a stirred solution of 3.2 g. (0.049 mole) of sodium azide in 100 ml. of water at 10-20°. Stirring was continued for 20 minutes after the addition was complete. Then, 200 ml. of water was added and the mixture was stirred for an additional 30 minutes, giving an oil (VIb); ir ν max (neat) cm^{-1}: 2130 (N_3), 1675 (C=O). This oil was extracted with 200 ml. of benzene. To the benzene solution, 100 ml. of water was added and the mixture was refluxed for 1.5 hours under vigorous stirring. The benzene layer was separated and dried over anhydrous sodium sulfate, and the benzene was removed *in vacuo* to leave red crystals. The red crystals were recrystallized from benzene to give red needles (VIIb), 6.5 g., m.p. 155-157°.

α-4-Bromophenyl-β-2-(5-nitrofuryl)vinylamine (VIIc).

A mixture of 11.3 g. (0.035 mole) of IVc, 6.2 g. (0.053 mole) of thionyl chloride and 70 ml. of benzene was refluxed for 1.5 hours, and the solvent was removed *in vacuo*. The oily residue (Vc) was dissolved in 100 ml. of acetone. A solution of Vc was added portionwise to a stirred solution of 3.4 g. (0.053 mole) of sodium azide in 100 ml. of water at 10-20°. Stirring was continued for 20 minutes after the addition was complete. Then, 200 ml. of water was added and the mixture was stirred for an additional 30 minutes, giving an oil (VIc); ir ν max (neat cm^{-1}: 2130 (N_3), 1675 (C=O). The oil was extracted with 200 ml. of benzene. To the benzene solution, 200 ml. of water was added and the mixture was refluxed for 1.5 hours under vigorous stirring. The benzene layer was separated and dried over anhydrous sodium sulfate, and the benzene was removed *in vacuo* to leave red crystals. The red crystals were recrystallized from benzene to give red needles (VIIc), 6.5 g., m.p. 173-174°.

α-4-Iodophenyl-β-2-(5-nitrofuryl)vinylamine (VIId).

A mixture of 2.5 g. (0.007 mole) of IVd, 5 g. (0.013 mole) of thionyl chloride and 30 ml. of benzene was refluxed for 3 hours, and the solvent was removed *in vacuo*. The oily residue (Vd) was dissolved in 50 ml. of acetone. A solution of Vd was added portionwise to a stirred solution of 0.6 g. (0.01 mole) of sodium azide in 50 ml. of water at 10-20°. Stirring was continued for 20 minutes after the addition was complete, then 100 ml. of water was added and the mixture was stirred for an additional 30 minutes. The precipitate was filtered (VId); ir ν max (neat) cm^{-1}: 2135 (N_3), 1675 (C=O). Compound VId was refluxed for 2 hours in water (200 ml.)-benzene (200 ml.). The benzene layer was separated and dried over anhydrous sodium sulfate, and the benzene was removed *in vacuo* to leave red crystals. The red crystals were recrystallized from benzene to give red needles (VIId), 1.5 g., m.p. 189-191°.

α-4-Methoxyphenyl-β-2-(5-nitrofuryl)vinylamine (VIIe).

A mixture of 2.7 g. (0.01 mole) of IVe, 2.2 g. (0.019 mole) of thionyl chloride and 30 ml. of benzene were refluxed for 2 hours, and the solvent was removed *in vacuo*. The oily residue (Ve) was dissolved in 20 ml. of acetone. A solution of Ve was added portionwise to a stirred solution of 0.9 g. (0.014 mole) of sodium azide in 20 ml. of water at 10-20°. Stirring was continued for 20 minutes after the addition was complete, then 100 ml. of water was added and the mixture was stirred for an additional 30 minutes, giving an oil (VIe); ir ν max (neat) cm^{-1}: 2140 (N_3), 1675 (C=O). The oil was extracted with 200 ml. of benzene. To a solution of VIe, 200 ml. of water was added and the mixture was refluxed for 3 hours under vigorous stirring. The benzene layer was separated and dried over anhydrous sodium sulfate, and the benzene was removed *in vacuo* to leave red crystals. The red crystals were recrystallized from methanol to give red needles (VIIe), 2 g., m.p. 178-179°.

α-4-Nitrophenyl-β-2-(5-nitrofuryl)vinylamine (VIIf).

A mixture of 9.2 g. (0.033 mole) of IVf, 4.2 g. (0.035 mole) of thionyl chloride and 50 ml. of benzene was refluxed for 5 hours and the solvent was removed *in vacuo*. The precipitated yellow crystals (Vf) were dissolved in 150 ml. of acetone. A solution of Vf was added portionwise to a stirred solution of 2.9 g. (0.45

mole) of sodium azide in 150 ml. of water at 10-20°. Stirring was continued for 20 minutes after the addition was complete. Then 300 ml. of water was added and the mixture was stirred for an additional 30 minutes, giving yellow crystals (VIf), m.p. 78-82° dec.; ir ν max (nujol) cm^{-1}: 2155 (N_3), 1675 (C=O). Compound VIf was refluxed for 1 hour in water (10 ml.)-dioxane (90 ml.), poured into ice water and filtered. The red precipitate was recrystallized from methanol to give dark red needles (VIIf), 5.5 g., m.p. 177-178°.

α-1-Naphthyl-β-2-(5-nitrofuryl)vinylamine (VIIg).

A mixture of 2.4 g. (0.008 mole) of IVg, 1.4 g. (0.012 mole) of thionyl chloride and 30 ml. of benzene was refluxed for 2 hours, and the solvent was removed *in vacuo*. The precipitated yellow crystals (Vg) were dissolved in 20 ml. of acetone. A solution of Vg was added portionwise to sodium azide in 20 ml. of water at 10-20°. Stirring was continued for 20 minutes after the addition was complete. Then, 150 ml. of water was added and the mixture was stirred for an additional 30 minutes, giving a yellow precipitate upon filtration (VIg), m.p. 97-99° dec.; ir ν max (nujol) cm^{-1}: 2150 (N_3), 1680 (C=O). Compound VIg was refluxed for 0.5 hour in water (5 ml.)-dioxane (45 ml.), poured into ice water and extracted with ether and dried over anhydrous sulfate. The ether was removed *in vacuo* to leave a dark red oil. The oil was chromatographed on silica gel (Wako gel C-200) with benzene as eluent. This procedure yielded red needles (VIIg), 0.6 g., m.p. 148-150°.

β-2-(5-Nitrofuryl)vinylurea (IXa).

A.

A mixture of 5 g. (0.027 mole) of β-2-(5-nitrofuryl)acrylic acid, 6.2 g. (0.03 mole) of phosphorus pentachloride and 30 ml. of benzene was refluxed for 30 minutes, poured into ice water and filtered. The precipitated chloride was dissolved in 50 ml. of acetone. A solution of acetone was added portionwise to a stirred solution of 1.8 g. (0.028 mole) of sodium azide in 50 ml. of water at 10-20°. Stirring was continued for 10 minutes after the addition was complete. Then, 50 ml. of water was added and the mixture was stirred for an additional 30 minutes, giving yellow crystals upon filtration (VIIIa), m.p. 110° dec.; ir ν max (nujol) cm^{-1}: 2140 (N_3), 1660 (C=O). Compound VIIIa was refluxed for 2 hours in water (10 ml.)-dioxane (10 ml.) and the solvent was removed *in vacuo*. The brown crystals were recrystallized from methanol to give red needles (IXa), 1 g., m.p. 211-212° dec.; ir ν max (nujol) cm^{-1}: 3340, 3445 (NH_2), 1730 (C=O); ms m/e: 197 (M^+).

Anal. Calcd. for $C_7H_7N_3O_4$: C, 42.64; H, 3.58; N, 21.32. Found: C, 42.55; H, 3.60; N, 21.35.

B.

Compound VIIIa, 3 g. (0.014 mole) was refluxed for 2 hours in 50 ml. of dried benzene. Ammonia gas was then bubbled into the benzene solution at room temperature. The precipitate was recrystallized from methanol to give red needles (IXa), 2.5 g., m.p. 211-212° dec. For compound XIa; ir ν max (neat) cm^{-1}: 2220 (N=C=O).

α-Methyl-β-2-(5-nitrofuryl)vinylurea (IXb).

A.

A mixture of 3 g. (0.015 mole) of α-methyl-β-2-(5-nitrofuryl)-acrylic acid, 5 g. (0.042 mole) of thionyl chloride and 30 ml. of benzene was refluxed for 2 hours, and the solvent was removed *in vacuo*. The precipitated chloride was dissolved in 30 ml. of acetone. A solution of acetone was added portionwise to a stirred solution of 1.4 g. (0.016 mole) of sodium azide in 20 ml. of water at 10-20°. Stirring was continued for 10 minutes after the addition was complete. Then, 50 ml. of water was added and the mixture was stirred for an additional 30 minutes, giving yellow crystals upon filtration (VIIIb), m.p. 94-95° dec.; ir ν max (nujol) cm^{-1}: 2150 (N_3), 1670 (C=O). Compound VIIIb was refluxed for 1 hour in water (10 ml.)-dioxane (90 ml.), poured into ice water and filtered. The red precipitate was recrystallized from methanol to give red needles (IXb), 0.8 g., m.p. 184-186° dec.; ir ν max (nujol) cm^{-1}: 3325, 3450 (NH_2), 1730 (C=O); ms m/e: 211 (M^+).

Anal. Calcd. for $C_8H_9N_3O_4$: C, 45.50; H, 4.30; N, 19.90. Found: C, 45.45; H, 4.11; N, 20.15.

B.

Compound VIIIb, 3 g. (0.015 mole) was refluxed for 2 hours in 50 ml. of dried benzene. Ammonia gas was then bubbled into the benzene solution at room temperature. The precipitate was recrystallized from methanol to give red needles (IXb), 2.2 g., m.p. 184-186° dec. For compound XIb; ir ν max (neat) cm^{-1}: 2220 (N=C=O).

2,4-Dinitrophenylmethyl Phenyl Ketone (XII).

α-Phenyl-β-2,4-dinitrophenylacrylic acid, 0.5 g. (0.0016 mole), was refluxed for 3 hours in 10 ml. of thionyl chloride and the solvent was removed *in vacuo*. The residue was dissolved in 50 ml. of acetone. A solution of acetone was added protionwise to a stirred solution of 0.11 g. (0.0017 mole) of sodium azide in 50 ml. of water at 10-20°. Stirring was continued for 10 minutes after the addition was complete. Then 100 ml. of water was added and the mixture was stirred for an additional 30 minutes, giving yellow crystals upon filtration (XII), m.p. 95-100° dec.; ir ν max (nujol) cm^{-1}: 2130 (N_3), 1670 (C=O). Compound XII was heated at 80-90° for 20 minutes, poured into ice water, extracted with ether and dried over anhydrous sodium sulfate. The ether was removed *in vacuo*, leaving a red oil. The red oil was chromatographed on silica-gel (Wako gel C-200) with benzene as eluent. This procedure yielded 0.3 g. of XIII, m.p. 134-135°; ir ν max (nujol) cm^{-1}: 1680 (C=O); nmr (δ ppm in deuteriochloroform): 4.93 (2H, s, CH_2), 9.07 (1H, d, J = 2.5 Hz, 3-H of nitrophenyl), 8.60 (1H, d-d, J = 2.5 Hz and J = 8.0 Hz, 5-H of nitrophenyl), 8.10, 7.70 (6H, each m, phenyl and 6-H of nitrophenyl); ms m/e: 186 (M^+).

Anal. Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.52; N, 9.79. Found: C, 58.55; H, 3.47; N, 10.02.

N-[α-Ethoxycarbonyl-β-2-(5-nitrofuryl)vinyl]pyridinium Bromide (XIVa).

A mixture of 3 g. (0.021 mole) of 5-nitro-2-furfural, 5 g. (0.021 mole) of *N*-ethoxycarbonylmethylpyridinium bromide, 0.5 ml. of pyridine and 50 ml. of acetic anhydride was heated at 30-40° for 3 hours. After cooling, the precipitate was filtered and recrystallized from ethanol to give yellow prisms (XIVa), 6.2 g., m.p. 270° (color change point).

Anal. Calcd. for $C_{14}H_{13}BrN_2O_5$: C, 45.54; H, 3.54; N, 7.59. Found: C, 45.33; H, 3.59; N, 7.45.

N-[α-Benzoyl-β-2-(5-nitrofuryl)vinyl]pyridinium Bromide (XIVb).

A mixture of 2 g. (0.014 mole) of 5-nitro-2-furfural, 3.9 g. (0.014 mole) of *N*-phenacylpyridinium bromide, 0.5 ml. of pyridine and 50 ml. of acetic anhydride was heated at 40-50° for 2 hours. After cooling, the precipitate was filtered and recrystallized from methanol to give yellow needles (XIVb), 5.5 g., m.p. 238-240°.

Anal. Calcd. for $C_{13}H_{11}BrN_2O_4$: C, 53.88; H, 3.27; N, 6.98. Found: C, 53.88; H, 3.15; N, 7.21.

N-[α-2-(5-Nitrofuryl)-β-2-(5-nitrofuryl)vinyl]pyridinium Bromide (XIVc).

A mixture of 0.5 g. (0.0035 mole) of 5-nitro-2-furfural, 1 g. (0.0035 mole) of *N*-2-(5-nitrofuryl)pyridinium bromide, 0.1 ml. of pyridine and 20 ml. of acetic anhydride was heated at 30-40° for 2 hours. After cooling, the precipitate was filtered and recrystallized from methanol-water (4:1) to give yellow prisms (XIVc), 1.3 g., m.p. 240° (color change point).

Anal. Calcd. for $C_{15}H_{10}BrN_3O_6$: C, 44.14; H, 2.47; N, 10.30. Found: C, 43.95; H, 2.33; N, 10.09.

α-Ethoxycarbonyl-β-2-(5-nitrofuryl)vinylamine (XVa).

To a stirred solution of 20 g. (0.061 mole) of XIVa in 100 ml. of ethanol, 25 ml. of morpholine was added at 0° and stirring was continued for 10 minutes at 0°. The mixture was poured into ice water and filtered. The precipitate was recrystallized from ethanol to give red bars (XVa), 5.5 g., m.p. 104-105°.

α-Benzoyl-β-2-(5-nitrofuryl)vinylamine (XVb).

To a stirred solution of 7.8 g. (0.019 mole) of XIVb in 50 ml. of methanol, 15 ml. of morpholine was added at 0° and stirring was continued for 10 minutes at 0°. The mixture was poured into ice water and extracted with 300 ml. of benzene. The benzene layer was separated and dried over anhydrous sodium sulfate, and the benzene was removed *in vacuo* leaving a brown oil. The oil was chromatographed on silica gel (Wako gel C-200) with benzene as eluent. This procedure yielded red prisms (XVb), 0.5 g., m.p. 93-94°.

α-2-(5-Nitrofuryl)-β-2-(5-nitrofuryl)vinylamine (XVc).

To a stirred solution of 1 g. (0.003 mole) of XIVc in 40 ml. of methanol, 5 ml. of piperidine was added at 0° and stirring was continued for 5 minutes at 0°. The mixture was poured into ice water and filtered. The precipitate was chromatographed on silica gel (Wako gel C-200) with benzene as eluent. This procedure yielded red needles (XVc), 0.15 g., m.p. 218-220°.

REFERENCES AND NOTES

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(7) Uv λ max (ethanol) nm (log ε): 261 (4.49), 428 (4.54).