103–104°, was obtained. Recrystallization from chloroform-heptane afforded yellow needles, m.p. 104.5–105.5°, $[\alpha]_D^{25}$ −32.8° (*c*, 0.2 in methanol).

Anal. Calcd. for $C_{12}H_{12}N_4O_8S$: C, 38.71; H, 3.25. Found: C, 38.58; H, 3.36.

5,5-Dimethyl-2-methylthio-2-oxazolinium picrate (IVb). Methylation of 0.5 g. of 5,5-dimethyl-2-thioöxazolidone[18] in absolute ethanol, as described above, gave 0.82 g. (57% yield) of picrate, m.p. 132–134°. Yellow prismatic crystals, m.p. 133–134.5°, were obtained on recrystallization from chloroform-heptane.

Anal. Calcd. for $C_{12}H_{14}N_4O_8S$: C, 38.50; H, 3.77; S, 8.56. Found: C, 38.64; H, 3.87; S, 8.54.

Thiazolinium picrates. When 2-thiothiazolidone was refluxed in ethanol with a slight excess of methyl iodide for 45 min., 2-methylthio-2-thiazoline was isolated as the picrate in 51% yield.[19] When the reactants were refluxed for 45 min. in the presence of sodium ethylate, the picrate was obtained in 84% yield.

The preparation of 2-methylthio-2-thiazoline by the cyclization of methyl 2-hydroxyethyldithiocarbamate has been reported by Crawhall and Elliott[20] and the melting point of the picrate given as 123°. The picrate obtained in this Laboratory, however, melted at 150–151°. Since the structures of the cyclization products involved are of considerable interest,[16,21] the preparation by the method of Crawhall and Elliott was repeated. The resulting picrate melted at 150–151°, and the products from the two methods were found to be identical.

The infrared spectrum of 2-methylthio-2-thiazolinium picrate showed the following bands and intensities: 2.84(w), 6.14(s), 6.21(vs), 6.39(vs), 6.45(vs), 6.58(s), 6.74(m), 6.97(m), 7.32(s), 7.51(s), 7.61(s), 7.95(vs), 8.65(s), 9.30(m), 9.52(m), 10.88(m), 11.00(m), 12.65(m), 13.46(m), 14.25(s), and 15.12(m) μ.

2-Ethylthio-2-thiazolinium picrate, prepared by ethylation under alkaline conditions, formed prismatic crystals, m.p. 112.5–114°, from aqueous acetone.

Anal. Calcd. for $C_{11}H_{12}N_4O_7S_2$: C, 35.10; H, 3.22. Found: C, 35.24; H, 3.30.

Infrared spectra. The spectra in the 2–8 μ region were obtained employing a Perkin-Elmer model 112, single beam, double pass infrared spectrophotometer equipped with calcium fluoride optics. In the 8 μ to 16 μ region spectra were obtained from a Baird model A, double beam infrared spectrophotometer using sodium chloride optics. All samples were run as potassium bromide disks with approximately equal weights of samples.

Acknowledgments. We wish to thank Dr. M. G. Ettlinger of The Rice Institute for his valuable suggestions and advice. We thank also Dr. J. D. Margerum and his associates of the Spectroscopy Section for assistance in determining the infrared spectra.

NATICK, MASS.

(18) H. A. Bruson and J. N. Eastes, *J. Am. Chem. Soc.*, 59, 2011 (1937).

(19) The preparation of 2-methylthio-2-thiazolinium iodide from 2-thiothiazolidone and methyl iodide in 87% yield by refluxing for 2 hr. in methanol has recently been reported by McKay, *et al.*[9]

(20) J. C. Crawhall and D. F. Elliott, *J. Chem. Soc.*, 3094 (1952).

(21) A. A. Rosen, *J. Am. Chem. Soc.*, 74, 2994 (1952).

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DEPARTMENT, RESEARCH DIVISION, ABBOTT LABORATORIES]

5-Nitro-2-furyl-substituted 1,3,4-Oxadiazoles, 1,3,4-Thiadiazoles, and 1,3,5-Triazines[1]

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The preparation of two new types of antibacterial nitrofurans is described. In these compounds antibacterial activity is shown for the first time to be present in 5-nitrofurans which are joined at the 2-position directly to a carbon atom in another heterocycle. Two systems of this type have been prepared. The first is one in which the atomic configuration C=N—N—C= is contained in a cyclic arrangement. This is found in the 1,3,4-oxadiazoles and 1,3,4-thiadiazoles. In the second type of system there is no C=N—N—C= arrangement in the heterocycle, but antibacterial activity is retained. This is represented by the 1,3,5-triazines described.

In 1944 Dodd and Stillman[1a] published their finding that furans with a nitro group in the 5-position possessed antibacterial activity. In a later paper[2] the generalization was made, that, in order to be effective *in vivo*, the 2-position of the 5-nitrofuran must be substituted by a group of the general type C=N—N—C=. An example is the semicarbazone of 5-nitro-2-furaldehyde. In subsequent years, the great bulk of work carried out in this area has followed along these lines, *e.g.* nitrofurfurylidene derivatives and their vinylogs.[3]

It has now been found that the C=N—N—C= system described by Dodd *et al.*,[2] may be incorporated in a heterocycle and still retain *in vivo* activity.[3a] Such a compound is described in general terms by structure I. Two groups of such com-

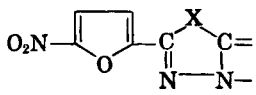
(1) Presented before the Division of Medical Chemistry, 136th Meeting, American Chemical Society, Atlantic City, N. J., September 13–18, 1959.

(1a) M. C. Dodd and W. B. Stillman, *J. Pharmacol. Exptl. Therap.*, 82, 11 (1944).

(2) M. C. Dodd, D. L. Cramer, and W. C. Ward, *J. Am. Pharm. Assoc.*, 39, 313 (1950).

(3) See, for example: K. Hayes, *J. Am. Chem. Soc.*, 77, 2333 (1955) and previous papers; H. Saikachi and H. Ogawa, *J. Am. Chem. Soc.*, 80, 3642 (1958).

(3a) Detailed information regarding the *in vitro* and *in vivo* antibacterial activity of these compounds will be published elsewhere.



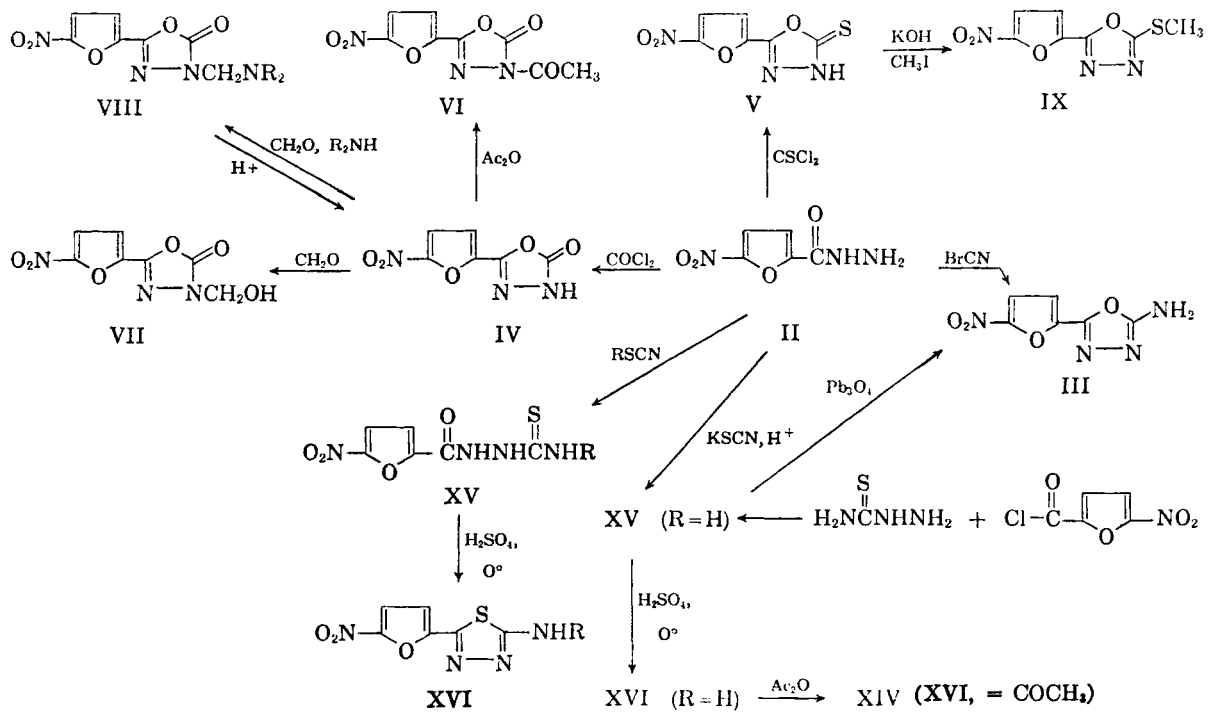
I

pounds will be described here, the 1,3,4-oxadiazoles where X = O and the 1,3,4-thiadiazoles where X = S. Perhaps more significant is the finding that certain compounds which do not contain the C=N—N—C= system at all, exhibit a high order of *in vitro* and *in vivo* activity.[3a] The nitrofuryl-1,3,5-triazines described here are examples of this type of compound.

1,3,4-Oxadiazoles. The semicarbazone of 5-nitro-2-furaldehyde was the first of the nitrofurans to have been used clinically. Although analogs and derivatives of the semicarbazone have been prepared, its structural features have never been incorporated into a heterocyclic system. This has now been done and the compound (III) found to be antibacterial both *in vitro* and in test animals. 2-Amino-5-(5-nitro-2-furyl)-1,3,4-oxadiazole (III) may be prepared by either of two routes. The preferable method is the recently described[4] reaction of cyanogen bromide with an acyl hydrazine. When 5-nitro-2-furoylhydrazine is treated with cyanogen bromide in refluxing ethanol the desired compound is formed. The aminooxadiazole may also be prepared, though in lower yield, by the general reaction[5] of an acyl thiosemicarbazide with red lead oxide in refluxing ethanol. The required 1-(5-nitro-2-furoyl)thiosemicarbazide is obtained either by the direct action of the acid chloride on thiosemicarbazide in dioxane, or by treating 5-nitro-2-furoylhydrazine with potassium thiocyanate in acidic solution.

When acyl hydrazines are treated with phosgene[6] or with thiophosgene,[7] 5-substituted 1,3,4-oxadiazole-2-ones or thiones are formed. Thus 5-nitro-2-furoylhydrazine and phosgene produce 5-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (IV). In a similar way thiophosgene gives rise to the 2-thione (V). The infrared spectrum[7a] of the oxadiazolone has a strong absorption at 5.64 μ (Nujol mull) supporting the keto structure IV, at least in the solid state. The thione has medium strength absorptions at 2.92 and 3.18 μ, and strong absorption from 7.53 to 7.63 μ (1.25% in chloroform). These maxima correspond closely to values assigned to 5-methyl-1,3,4-oxadiazol-2-thione by Ainsworth[8] (2.90 N—H, monomer; 3.16 N—H dimer; 7.57 C=S dimer; 7.65 C=S monomer; all in chloroform). Ainsworth found that the methyl oxadiazolthione existed in both monomeric and dimeric states, the dimer being hydrogen-bonded thiocarbonyl to N—H. It appears that V is similar in this respect although the 7.53–7.63 region is poorly resolved due to interfering C—NO_2 absorption.

A monoacetyl derivative is obtained on treat-



(4) A. P. Swain, U. S. Patent 2,883,391 (1959).

(5) R. Stollé and K. Fehrenbach, *J. prakt. Chem.*, 122, 289 (1929).

(6) A. Dornow and K. Bruncken, *Ber.*, 82, 121 (1949).

(7) E. Hoggarth, *J. Chem. Soc.*, 4811 (1952).

(7a) Infrared spectra were determined by W. Washburn, of Abbott Laboratories, whose aid in the interpretation of this data is acknowledged. Spectra were measured on a Perkin-Elmer model 21 spectrophotometer.

(8) C. Ainsworth, *J. Am. Chem. Soc.*, 78, 4475 (1956).

ment of IV with hot acetic anhydride. This appears to be the *N*-acetyl compound VI for the infrared spectrum contains two carbonyl absorptions, one at 5.50μ, the other at 5.70 μ (2.3% in chloroform), eliminating the possibility of *O*-acetylation.

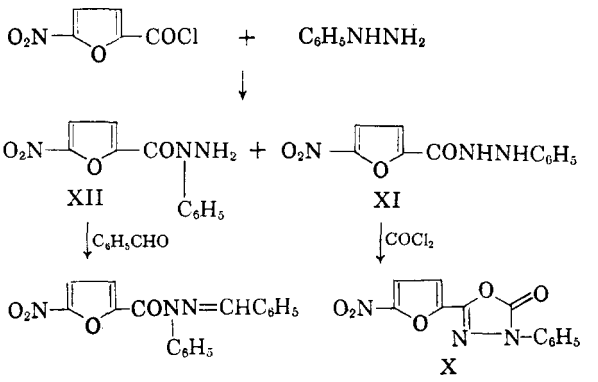
1,3,4-Oxadiazol-2-ones are known to undergo the Mannich reaction, giving rise to 3-hydroxymethyl or aminomethyl derivatives in the usual way.[9] Utilizing this reaction, the 3-hydroxymethyl (VII) and several 3-aminomethyl oxadiazolones (VIII) were obtained. The group included Mannich bases derived from dimethylamine, diethylamine piperidine, morpholine, pyrrolidine, hexamethyleneimine, and the bisnitrofuryloxadiazolylcompound from piperazine. All of these compounds were easily obtained except the hydroxymethyl derivative VII which was isolated only with difficulty, and in poor yield. The Mannich bases thus obtained were similar to those previously reported[9b] in their ready decomposition by acid to the parent compound IV.

If the thione V is treated with methyl iodide in alcohol potassium hydroxide a monomethyl derivative is formed. This is probably the methylthio compound IX since the infrared spectrum in chloroform solution does not show the presence of N—CH_3 and there is marked attenuation of the absorption in the 7.5 to 7.6 μ region (see above). Treatment of the thione V with mercuric oxide in either refluxing water or dioxane resulted only in the isolation of the bis salt with mercury. This procedure has been used[10] to convert oxadiazolthiones to oxadiazolones, and was expected to give rise to IV.

Another procedure which was expected to lead to the oxadiazolone IV was the treatment of the methylthio compound IX with aqueous acid. However when IX was heated with concentrated hydrochloric acid more extensive hydrolysis occurred, and only 5-nitro-2-furoic acid was isolated.

The most active member of this series in animals is the nitrofuryloxadiazolone IV. This compound and its acid-labile Mannich derivatives are effective against Gram positive and negative infections in animals by both intramuscular and oral routes. In view of the high activity of the oxadiazolone, it was surprising that the thione V had no activity either *in vitro* or *in vivo*.

Similarly inactive was 3-phenyl-5-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (X) obtained by the action of phosgene on 1-(5-nitro-2-furoyl)-2-phenylhydrazine (XI). Compound XI was obtained along with 1-(5-nitro-2-furoyl)-1-phenylhydrazine (XII) by treating phenylhydrazine with nitrofuroyl chloride in either benzene or diethyl ether. When the reaction was carried out in benzene the product ratio was 37.8% XII to 17.4% XI, while in diethyl ether the ratio was reversed, giving 16.2% XII and 58.2% XI. The structure of XII was established by conversion to its benzylidene derivative.



The reaction of nitrofuroyl chloride with phenylhydrazine to produce both XI and XII is somewhat unusual. For example treatment of phenylhydrazine with benzoyl chloride gives 1-benzoyl-2-phenylhydrazine in the cold[11] or 1,2-dibenzoylphenylhydrazine in hot benzene.[12] Only when the sodio derivative of phenylhydrazine is treated with benzoyl chloride is the 1-benzoyl-1-phenylhydrazine formed[13] and this is accompanied by 2-benzoyl and 1,2-dibenzoyl phenylhydrazine.

1,3,4-Thiadiazoles. A procedure which has been shown to be general for the preparation of 1,3,4-thiadiazoles is the cyclization of 1-acylthiosemicarbazides by cold concentrated sulfuric acid.[14] Using this method several 5-(5-nitro-2-furyl)-1,3,4-thiadiazoles were prepared. In this way 1-(5-nitro-2-furoyl)thiosemicarbazide (XV, R=H) was cyclized to 2-amino-5-(5-nitro-2-furyl)-1,3,4-thiadiazole (XVI, R=H) in good yield. Similar treatment of 1-(5-nitro-2-furoyl)-4-alkyl-(or -aryl)-thiosemicarbazides gives rise to the 1-(5-nitro-2-furoyl)-4-substituted amino thiadiazoles. In this way were obtained the compounds XVI in which R is methyl, ethyl, and phenyl. The required 1-nitrofuroyl-4-substituted thiosemicarbazides (XV) were obtained by the action of isothiocyanates on nitrofuroylhydrazine (II).

The nitrofurylaminothiadiazole XVI (R=H) was the most active antibacterial of the thiadiazoles tested, being effective in animals when administered by either oral or intramuscular routes. The substituted amino derivatives showed decreasing activity in the order R=CH_3>C_2H_5>C_6H_5.

1,3,5-Triazines. The condensation of esters of heterocyclic acids with biguanide or substituted biguanides provides a convenient route to amino- or substituted aminotriazines.[15] Methyl 5-nitro-2-furoate reacts in this way to produce 2,4-di-

(9)(a) A. Dornow and S. Lüpfert, *Arch. Pharm.*, **288**, 311 (1955). (b) H. C. Caldwell, R. J. Seiwald, and J. H. Burckhalter, *J. Am. Pharm. Assoc.*, **477**, 799 (1958).

(10) See for example: M. Freund and B. B. Goldsmith, *Ber.*, **21**, 1240, 2456 (1888).

(11) E. Fischer, *Ann.*, **190**, 67 (1878).

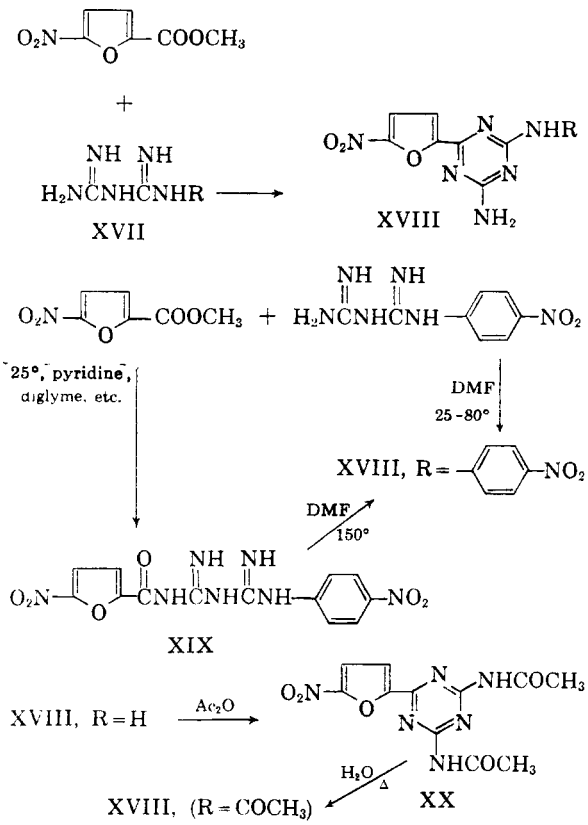
(12) H. Franzen, *Ber.*, **42**, 2465 (1909).

(13) A. Michaelis and F. Schmidt, *Ann.*, **252**, 300 (1889).

(14) E. Hoggarth, *J. Chem. Soc.*, 1163 (1949).

(15) J. T. Thurston and D. W. Kaiser, U. S. Patent 2,535,968 (1950).

amino-6-(5-nitro-2-furyl)-1,3,5-triazine[16] (XVIII, R = H). This compound was found to have a high degree of antibacterial activity in animals when administered by the intramuscular route. This is the first example of a systemically effective antibacterial which does not contain the —C=N—N—C= system felt by Dodd[2] to be requisite for *in vivo* activity. Several substituted amino derivatives of this compound have now been prepared and found to be less active in general than the parent compound (XVIII, R = H).



When methyl 5-nitro-2-furoate is allowed to react with 1-substituted biguanides (XVII, R = isopropyl, phenyl, *o*-tolyl, *p*-chlorophenyl, *p*-nitrophenyl) the 2-amino-4-substituted amino-6-(5-nitro-2-furyl)-1,3,5-triazines (XVIII, R as above) are formed. The yields from this reaction are very low (see Experimental); however, this appears to be the most useful route to these compounds. In one attempt to prepare XVIII (R = *o*-tolyl) using nitrofuroyl chloride and *o*-tolylbiguanide no cyclized product was obtained.

A possible explanation of the low yields of the substituted aminotriazines compared with the yields obtained in the preparation of the parent compound may lie in the very slow rate of product formation when substituted biguanides are used. While XVIII (R = H) was formed in 80% yield after reacting overnight at room temperature, the substituted biguanides required from three to five days for reaction. Long standing in solution with the basic biguanides could destroy large amounts of the base-labile nitrofuran intermediates or products. The reduced rates of cyclization may result from a combination of steric and electric effects.

When *p*-nitrophenylbiguanide (XVII, R = *p*-nitrophenyl) is treated with methyl nitrofuroate at room temperature in pyridine, diethylene glycol dimethyl ether, or ethylene glycol monomethyl ether, or in refluxing ethanol, an intermediate is formed which apparently is 1-(5-nitro-2-furoyl)-5-(*p*-nitrophenyl)biguanide (XIX). The compound is isolated only as a monohydrate, and attempts to remove the molecule of water have been unsuccessful. The identity as XIX rests on the combustion analysis of the hydrate and the fact that the intermediate may be cyclized to the triazine (XVIII, R = *p*-nitrophenyl) by short boiling in dimethylformamide. If dimethylformamide is used as solvent and the reaction carried out either at room temperature or by warming on a steam bath, the triazine is obtained directly, without isolation of intermediate XIX. This appears to be due to the much greater solubility of XIX in dimethylformamide than in other solvents. When the other solvents were used, the intermediate separated and because of its low solubility did not react further. In dimethylformamide, however, the material remained in solution, facilitating cyclization.

2,4-Diamino-6-(5-nitro-2-furyl)-1,3,5-triazine (XVIII, R = H) is a weakly basic compound of low solubility in most solvents. It is stable toward warm concentrated hydrochloric acid, but does not form a stable hydrochloride salt. Warm 10% sodium hydroxide decomposes the compound. When refluxed with acetic anhydride a diacetyl derivative is formed (XX), which is converted to the monoacetyl derivative (XVIII, R = $COCH_3$) by boiling for sixteen hours in water.

EXPERIMENTAL[17]

2-Amino-5-(5-nitro-2-furyl)-1,3,4-oxadiazole (III). *Procedure A.* 5-Nitro-2-furoylhydrazine[18] (68.4 g., 0.4 mole) and cyanogen bromide (48.0 g., 0.45 mole) were heated together under reflux in 2000 ml. of methanol for 1 hr. Cooling provided about 20.4 g. of crude product, m.p. 250–255°. On concentration of the mother liquor a brown oil was obtained, which, when poured into 500 ml. of water produced an additional 30 g. of crude product (m.p. 240–249°). The total yield of crude product was 50.4 g. or 64% of theory. Crystallization from dimethylformamide-ethanol gave yellow needles, m.p. 258–260° dec.

Procedure B. A mixture of 1-(5-nitro-2-furoyl)thiosemicarbazide (4.60 g., 0.02 mole) and red lead oxide (Pb_3O_4)

(16) R. U. Schock and A. Alter, unpublished results from Abbott Laboratories; R. U. Schock, U. S. Patent 2,885,400 (May 5, 1959).

(17) All melting points are uncorrected and were determined in capillary tubes.

(18) H. L. Yale, *et al.*, *J. Am. Chem. Soc.*, 75, 1933 (1953).

(34.2 g., 0.05 mole) was heated with stirring in 250 ml. of boiling ethanol. After 24 hr. the suspension was filtered and the solid residue extracted three times with hot alcohol. On concentration of the alcoholic extracts the product separated as fine yellow needles, m.p. 260.5° dec., weighing 0.64 g. (16%). Recrystallization as above gave material, m.p. 261.5° dec.

Anal. Calcd. for $C_6H_4N_4O_4$: C, 36.74; H, 2.06. Found: C, 36.84; H, 2.12.

5-(5-Nitro-2-furyl)-1,3,4-oxadiazol-2-one (IV). A solution of 5-nitro-2-furoylhydrazine (50.15 g., 0.30 mole) in 500 ml. of dilute (10:1) hydrochloric acid was stirred with cooling while phosgene was introduced beneath the surface of the liquid. After 1 hr. the product was collected by filtration and washed with water. This gave 54 g. (92%) of light tan-colored platelets, m.p. 200–202° dec. Crystallization from acetone-water gave material melting at 201–202° dec. Repeated crystallization lowered the melting point.

Anal. Calcd. for $C_6H_3N_3O_5$: C, 36.56; H, 1.52; O, 40.59. Found: C, 36.36; H, 1.80; O, 40.36.

5-(5-Nitro-2-furyl)-1,3,4-oxadiazol-2-thione (V). To a suspension of 5-nitro-2-furoylhydrazine (17.11 g., 0.1 mole) in 375 ml. of dioxane was added thiophosgene (11.5 g., 0.1 mole) at room temperature. After the mildly exothermic reaction had ended the solution was treated with charcoal and filtered. The solution was diluted with 700 ml. of hexane, cooled, and seeded or scratched to produce 13.40 g. of yellow product, m.p. 154–155° dec. (64%). This may be crystallized from boiling water to give yellow needles, m.p. 157.5–158° dec.; however, the recovery is only 65%. This compound is soluble in chloroform, alcohols, acetone, etc., and in dilute potassium carbonate, from which it precipitates unchanged on acidification.

Anal. Calcd. for $C_6H_3N_3O_4S$: C, 33.81; H, 1.42; N, 19.72; S, 15.01. Found: C, 34.04; H, 1.59; N, 19.67; S, 15.01.

3-Acetyl-5-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (VI). Compound IV (10 g., 0.51 mole) was covered with acetic anhydride and heated under reflux for 2 hr. The solution was taken to dryness *in vacuo* and the residue crystallized from acetone-water to give 10.22 g. (84%) of light yellow crystals, m.p. 143–144°. Two recrystallizations as above gave product, m.p. 144–144.5°.

Anal. Calcd. for $C_8H_5N_3O_6$: C, 40.18; H, 2.11; N, 17.57. Found: C, 39.98; H, 1.98; N, 17.41.

3-Hydroxymethyl-5-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (VII). A mixture of IV (9.85 g., 0.05 mole), formalin (3.75 ml., 0.05 mole), and 40 ml. of water was heated to boiling and then warmed on a steambath for 30 min. On cooling, an oil separated which on long standing produced a few crystals of product. The crystals were collected and crystallized from ethanol-cyclohexane giving white needles, m.p. 110–111°, weighing 0.54 g. (4.7%).

Anal. Calcd. for $C_7H_5N_3O_6$: C, 37.01; H, 2.22; O, 42.27. Found: C, 37.12; H, 2.62; O, 41.95.

3-Dimethylaminomethyl-5-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (VIIIa). To a stirred, ice cold suspension of IV (19.7 g., 0.1 mole) in 200 ml. of absolute ethanol was added formalin (7.5 ml., 0.1 mole) followed by an alcoholic solution of dimethylamine (30 ml. of 0.15 g./ml., 0.1 mole). A deep red solution formed which soon began to precipitate orange crystals. After 10 min. the material was collected by filtration. Following crystallization from alcohol, this weighed 14 g. and melted 117–147°. When this was extracted with 800 ml. of hot benzene, a residue (partly of starting material, partly of unknown composition) remained. Evaporation of the benzene filtrate to 100 ml. and cooling gave 7.1 g. (28%) of VIIIa, m.p. 118–119°.

Anal. Calcd. for $C_9H_{10}N_4O_5$: C, 42.52; H, 3.97; N, 22.04. Found: C, 42.68; H, 3.93; N, 22.02.

3-Diethylamino-5-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (VIIIb). A hot solution of IV (19.71 g., 0.1 mole) in 200 ml. of absolute alcohol containing 10 ml. of dimethylformamide was cooled to 40° and formalin (7.5 ml., 0.1 mole) and diethylamine (7.31 g., 0.1 mole) added. The solution was cooled in an ice bath and crystallization induced by scratching. The yellow product obtained weighed 6.08 g. (22%) and melted at 99–99.5°. VIIIb is soluble in carbon tetrachloride, benzene, alcohols, *etc.* slightly soluble in water, and insoluble in cyclohexane, *etc.* Recrystallization from solvents or solvent pairs could not be achieved.

Anal. Calcd. for $C_{11}H_{14}N_4O_5$: C, 46.81; H, 5.00; O, 28.35. Found: C, 46.59; H, 5.03; O, 28.62.

3-Piperidinomethyl-5-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (VIIIc). The general procedure outlined above for VIIIb was followed using piperidine (8.52 g., 0.1 mole). The product separated directly as flat orange needles, m.p. 134.5–135°, weighing 23.00 g. (78.2% of theory). Crystallization from ethanol gave yellow crystals, m.p. 133.5–134°.

Anal. Calcd. for $C_{12}H_{14}N_4O_5$: C, 48.98; H, 4.80; N, 19.04. Found: C, 49.10; H, 4.98; N, 19.25.

3-Morpholinomethyl-2-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (VIIId). The general procedure outlined above for VIIIa was followed using morpholine (8.71 g., 0.1 mole). Cooling gave 27.4 g. (93%) of yellow crystals, m.p. 191.5–192.5°. Crystallization from dimethylformamide-alcohol lowered the melting point to 190–191°.

Anal. Calcd. for $C_{11}H_{12}O_6N_4$: C, 44.60; H, 4.08; N, 18.91. Found: C, 44.77; H, 4.27; N, 18.85.

3-Pyrrolidinomethyl-5-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (VIIIe). The general procedure outlined above for VIIIb was followed using pyrrolidine (7.11 g., 0.1 mole). Cooling provided 23.8 g. (85%), m.p. 137–138° (140–141° preheated). Crystallization from dimethylformamide-ethanol gave material, m.p. 138–139°.

Anal. Calcd. for $C_{11}H_{12}N_4O_5$: C, 47.14; H, 4.32; O, 28.55. Found: C, 47.20; H, 4.60; O, 28.82.

3-Hexamethyleneiminomethyl-5-(5-nitro-2-furyl)-1,3,4-oxadiazol-2-one (VIIIf). The general procedure outlined above for VIIIb was followed using hexamethyleneimine (9.92 g., 0.1 mole). Cooling gave 28.3 g. of crystalline yellow product (92%), m.p. 134–135°.

Anal. Calcd. for $C_{13}H_{16}N_4O_5$: C, 50.64; H, 5.23; N, 18.18. Found: C, 50.79; H, 5.45; N, 18.32.

1,4-Bis[5-(5-nitro-2-furyl)-2-keto-1,3,4-oxadiazolyl-3-methyl]piperazine (VIIIg). The general procedure outlined above for VIIIb was employed using piperazine (4.31 g., 0.05 mole). The product separated immediately as an orange powder, m.p. 200° dec., weighing 23.9 g. (95%).

Anal. Calcd. for $C_{18}H_{16}N_8O_{10}$: C, 42.86; H, 3.70. Found: C, 42.82; H, 3.35.

Decomposition of the Mannich bases by acid. A suspension of VIIIe (0.85 g., 0.003 mole) in 10 ml. of water was treated with concd. hydrochloric acid (0.25 ml., 0.003 mole) with stirring. Almost immediately the color of the starting material changed from orange to tan. The product was collected and found to weigh 0.60 g. (94%) and to melt at 196–198.5°. A mixture of the product and IV melted at 198–199°. The infrared spectra (Nujol mull) of the product and IV were identical. Compounds VIIId and VIIIf behaved in the same way as VIIIe.

2-Methylthio-5-(5-nitro-2-furyl)-1,3,4-oxadiazole (IX). To a solution of V (6.39 g., 0.030 mole) in 30 ml. of ethanol was added 6 ml. of methyl iodide and a solution of potassium hydroxide (1.68 g., 0.030 mole) in 75 ml. of ethanol. The product separated almost immediately, providing 5.82 g. (85%) of fine yellow needles, m.p. 164.5–165°. Crystallization from dimethylformamide-water gave material melting 165.5–166°, with 93% recovery.

Anal. Calcd. for $C_7H_5N_3O_4S$: C, 37.01; H, 2.22. Found: 36.95; H, 2.36.

Reaction of V *with mercuric oxide.* A suspension of yellow mercuric oxide (1.73 g., 0.008 mole) and V (0.852 g., 0.004 mole) in 50 ml. of pure, dry dioxane was heated under reflux for 15 hr. The suspension was then filtered and the cake extracted with hot dimethylformamide. Addition of water to the extract gave a bright yellow precipitate, m.p. 260.5° dec., weighing 0.70 g. (56%). Recrystallization from dimethylformamide-water brought the m.p. to 262° dec.

This reaction was also carried out in boiling water for a similar length of time, providing the same product.

Anal. Calcd. for $C_{12}H_4N_6O_8S_2Hg$: C, 23.06; H, 0.65; N, 13.45; S, 10.22. Found: C, 23.75; H, 0.67; N, 13.65; S, 10.02; Hg, present (qualitative, by emission spectrum).

Reaction of IX *with hydrochloric acid.* A mixture of IX (0.90 g., 0.004 mole) and 20 ml. of concd. hydrochloric acid was heated on a steam bath for 7 hr. During this time, solution occurred and the odor of methyl mercaptan was detected. On cooling 0.46 g. (74%) of light yellow crystal separated, m.p. 182–183° dec. This was shown to be 5-nitro-2-furoic acid by a mixture melting point determination (undepressed) with authentic material obtained by the acid hydrolysis[19] of methyl 5-nitro-2-furoate.[20]

1-(5-Nitro-2-furoyl)-1-phenylhydrazine (XII) *and 1-(5-Nitro-2-furoyl)-2-phenyl-hydrazine* (XI). *Procedure A.* To a stirred, ice-cold solution of phenylhydrazine (4.32 g., 0.04 mole) in 25 ml. of dry benzene was added, dropwise, a solution of 5-nitro-2-furoyl chloride[21] in 25 ml. of dry benzene. After the addition the suspension was heated under reflux for a few minutes, cooled, and the product collected by filtration. The residue was washed with water and crystallized from absolute ethanol. Cooling provided 1.87 g. (37.8%) of XII, as yellow crystals, m.p. 167–167.5°. The alcohol mother liquor was then taken to dryness and the residue extracted with warm water and then crystallized from toluene. In this way yellow-orange needles of XI were obtained, m.p. 127.5–128°, weighing 0.86 g. (17.4%).

Anal. Calcd. for $C_{11}H_9N_3O_4$: C, 53.44; H, 3.67. Found XII: C, 53.68; H, 3.71. Found XI: C, 53.35; H, 3.68.

Compounds XI *and* XII, *Procedure B.* A solution of 5-nitro-2-furoyl chloride (3.51 g., 0.02 mole) in 50 ml. of dry ether was added slowly to a stirred, ice cold solution of phenylhydrazine (4.32 g., 0.04 mole) in 50 ml. of dry ether. The resulting suspension was filtered and the filtrate saved. The cake was washed with water and the residue dissolved in ethanol. On cooling XII separated weighing 0.80 g. (16.2%), m.p. 163–164°. The ethanol mother liquor was combined with the ether filtrate and the solvents removed. The residue was crystallized as before to give 2.87 g. (58.2%) of XI, m.p. 124.5–125.5°.

5-(5-Nitro-2-furyl)-3-phenyl-1,3,4-oxadiazol-2-one (X). A solution of XI (1.80 g., 0.0073 mole) in 50 ml. of toluene was heated on a steam bath and phosgene bubbled through the solution for 1 hr. The toluene was then removed in an air stream and the residue slurried in 25 ml. of boiling ethanol to give 1.42 g. (71.2%) of X, m.p. 186–187°. An additional 0.26 g., m.p. 184–185° was obtained from the alcohol mother liquor (total yield 84%). The product was soluble in acetone, chloroform, slightly soluble in ethanol and insoluble in hexane. For analysis, X was crystallized from toluene, raising the melting point to 186.5–187.5°.

Anal. Calcd. for $C_{12}H_5N_3O_5$: C, 52.56; H, 2.94; N, 15.33. Found: C, 52.48; H, 2.74; N, 15.18.

1-Benzylidene-2-(5-nitro-2-furoyl)-2-phenylhydrazine. Freshly distilled benzaldehyde (5 ml.) and XII (0.5 g., 0.002 mole) were heated together on a steam bath for 40 min. On cooling, 0.53 g. (78%) of the benzylidine derivative separated, m.p. 207–208°. Crystallization from toluene gave bright yellow crystals of the same melting point.

Anal. Calcd. for $C_{18}H_{13}N_3O_4$: C, 64.47; H, 3.91; N, 12.53. Found: C, 64.65; H, 4.16; N, 12.24.

1-(5-Nitro-2-furoyl)thiosemicarbazide (XV, R = H) *Procedure A.* A solution of 5-nitro-2-furoyl chloride (5.27 g., 0.03 mole) in 30 ml. of pure, dry dioxane was added slowly to a stirred suspension of thiosemicarbazide (2.73 g., 0.03 mole) and 7 g. of sodium bicarbonate in 50 ml. of dry dioxane. After the addition, the mixture was stirred for 2 hr. at room temperature and then heated on a steam bath for 10 min., cooled, and filtered. The filtered solution was reduced in volume and the product precipitated by addition of ethanol. In this way was obtained 3.15 g. (46% of theory) of XV (R = H), m.p. 186° (dec.). Crystallization from ethanol raised the melting point to 192° (dec.).

Procedure B. A mixture of 5-nitro-2-furoylhydrazine (34.22 g., 0.20 mole), potassium thiocyanate (25 g., 0.26 mole), concd. hydrochloric acid (20 ml.) and 300 ml. of water was heated for 4 hr. on a steam bath. After cooling overnight a dark brown solid had precipitated which was collected by filtration and slurried in a small amount of boiling ethanol for a few minutes. This provided 22.8 g. (50% of theory) of yellow XV (R = H), m.p. 186° dec.

Anal. Calcd. for $C_6H_6N_4O_4S$: C, 31.31; H, 2.63; N, 24.35. Found: C, 31.45; H, 2.97; N, 24.32.

4-Methyl-1-(5-nitro-2-furoyl)thiosemicarbazide (XV, R = CH_3). A solution of 5-nitro-2-furoylhydrazine (17.11 g., 0.10 mole) and methylisothiocyanate (8.04 g., 0.11 mole) in 250 ml. of ethanol was heated under reflux for 2 hr. Cooling gave 24.0 g. (96%) of material, m.p. 163–164° (when heated slowly from 110°). Crystallization from ethanol gave white needles, m.p. 166.5–167° (slow heating). This appeared to be XV (R = CH_3) solvated with one molecule of ethanol. Heating *in vacuo* at 100° gave the unsolvated product although in a somewhat discolored state. When this was heated slowly from 145°, it decomposed at 190°C.

Anal. Calcd. for $C_7H_8N_4O_4S \cdot C_2H_5OH$: C, 37.24; H, 4.86. Found: C, 37.22; H, 5.03.

Anal. Calcd. for $C_7H_8N_4O_4S$: C, 34.43; H, 3.30; N, 22.95. Found: C, 34.47; H, 3.27; N, 22.72.

4-Ethyl-1-(5-nitro-2-furoyl) thiosemicarbazide (XV, R = C_2H_5). This was prepared in the same way as XV (R = CH_3) above using ethyl isothiocyanate (9.59 g., 0.11 mole). In this way 23.45 g. (88%) of XV (R = C_2H_5) was obtained, m.p. 189–190°. Crystallization from ethanol gave pale yellow needles, m.p. 193°.

Anal. Calcd. for $C_8H_{10}N_4O_4S$: C, 37.21; H, 3.90; S, 12.41. Found: C, 37.49; H, 4.10; S, 12.35.

4-Phenyl-1-(5-nitro-2-furoyl)thiosemicarbazide (XV, R = C_6H_5). This was prepared as above for XV (R = CH_3) using phenyl isothiocyanate (14.90 g., 0.11 mole) and 350 ml. of ethanol. The mixture was heated for 30 min. under reflux. Cooling gave 26 g. (81%) of XV (R = C_6H_5), m.p. 174° dec. Crystallization from acetone-water gave yellow crystals, m.p. 175° dec.

Anal. Calcd. for $C_{12}H_{10}N_4O_4S$: C, 47.06; H, 3.29; N, 18.30. Found: C, 47.13; H, 3.48; N, 18.59.

2-Amino-5-(5-nitro-2-furyl)-13,4-thiadiazole (XVI, R = H). Concentrated sulfuric acid was cooled to 0° and stirred while XV (R = H) (11.51 g., 0.05 mole) was added portionwise. The mixture was stirred for 1 hr. in the cold and then allowed to warm to room temperature over a 1-hr. period. The solution was filtered to remove a small amount of insoluble material and then poured onto cracked ice and allowed to stand overnight in the cold. The precipitated yellow product was then crystallized from dimethylformamide-water giving 7.30 g. of olive-yellow material, m.p. 278° dec. An additional 0.76 g. was obtained by neutralizing the sulfuric acid solution. The total yield was 76%. Recrys-

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(20) H. Gilman and G. F. Wright, *J. Am. Chem. Soc.*, **52**, 2550, 4165 (1930).

(21) The nitrofuroyl chloride was obtained in 69% yield from nitrofuroic acid by heating under reflux with thionyl chloride for 20 hr. Under these conditions, a 24% yield of 5-nitro-2-furoic anhydride is also obtained. This compound, which has not been previously reported, is insoluble in cold thionyl chloride and thus is easily separated from the soluble acid chloride. It melts at 212–213° and crystallizes in light yellow needles from nitromethane. The infrared spectrum contains two strong absorptions at 5.59 and 5.76 μ (Nujol) which correspond well with known anhydride carbonyl absorptions. *Anal.* Calcd. for $C_{10}H_4N_2O_9$: C, 40.55; H, 1.36; N, 9.46. Found: C, 40.48; H, 1.53; N, 9.65.

If the acid and thionyl chloride were refluxed for 36 hr. only the acid chloride was obtained in 81% yield.

tallization as above for analysis gave yellow needles, m.p. 280° dec.

Anal. Calcd. for $C_5H_4N_4O_3S$: C, 33.97; H, 1.90; N, 26.42; O, 22.62. Found: C, 34.05; H, 2.20; N, 26.52; O, 22.35.

2-Methylamino-5-(5-nitro-2-furyl)-1,3,4-thiadiazole (XVI, R = CH_3). Compound XV (R = CH_3) ethanolate (3.37 g., 0.012 mole) was added in one portion to 50 ml. of stirred concd. H_2SO_4 at 0°. After solution occurred, the mixture was allowed to warm to room temperature and then poured onto ice. The solution was adjusted to *p*H 5 and the precipitated product collected. This provided 1.37 g. (52% of theory) of XVI (R = CH_3), m.p. 213–214° (dec.). Crystallization from dimethylformamide-water gave yellow cubes, m.p. 214.5–215.5° dec.

Anal. Calcd. for $C_7H_6N_4O_3S$: C, 37.14; H, 2.67; N, 24.78. Found: C, 37.38; H, 2.97; N, 24.66.

2-Ethylamino-5-(5-nitro-2-furyl)-1,3,4-thiadiazole (XVI, R = C_2H_5). This was prepared by the method described above for XVI (R = CH_3) only using XV (R = C_2H_5) (15.48 g., 0.06 mole). The crude orange solid obtained in this way weighed 13.74 g., m.p. 195–196° dec. Crystallization from dimethylformamide-water gave yellow felted needles, m.p. 216–216.5° dec., weighing 10.00 g. (70%).

Anal. Calcd. for $C_8H_8N_4O_3S$: C, 40.00; H, 3.36; N, 23.33. Found: C, 39.76; H, 3.40; N, 23.39.

2-Anilino-5-(5-nitro-2-furyl)-1,3,4-thiadiazole (XVI, R = C_6H_5). This was prepared in the same way as XVI (R = CH_3) using XV (R = C_6H_5) (18.38 g., 0.06 mole). The product was crystallized from dimethylformamide-water to give 12.63 g. (73%) of flat yellow needles, m.p. 264° (preheated). Recrystallization raised the melting point to 267–267.5° (preheated).

Anal. Calcd. for $C_7H_6N_4O_3S$: C, 50.00; H, 2.80; S, 11.12. Found: C, 49.98; H, 3.10; S, 11.12.

2-Acetylamino-5-(5-nitro-2-furyl)-1,3,4-thiadiazole (XIV). A solution of XVI (R = H) (7.0 g., 0.033 mole) and 8 ml. of acetic anhydride in 200 ml. of pyridine was maintained at 80–90° for 2 hr. Cooling caused the product to separate. After crystallization from pyridine, it melted at 308° dec. and weighed 8 g. (95%).

Anal. Calcd. for $C_8H_6N_4O_4S$: C, 37.79; H, 2.39; N, 22.04. Found: C, 37.72; H, 2.48; N, 22.08.

4-Amino-6-isopropylamino-2-(5-nitro-2-furyl)-1,3,5-triazine (XVIII, R = $CH[CH_3]_2$). Sodium metal (1.15 g., 0.05 g.-atom) was allowed to react with 50 ml. of dry ethylene glycol monomethyl ether. 1-Isopropyl biguanide hydrochloride[22] (8.98 g., 0.05 mole) was then added, the resulting sodium chloride filtered, and methyl 5-nitro-2-furoate (8.55 g., 0.05 mole) introduced. After standing for 3 days at room temperature, the product was collected by filtration and washed with ethanol, providing 2.73 g., m.p. 192.5–194°. After standing 2 weeks longer, the reaction mother liquor was taken to dryness and the residue was extracted with hot ethanol. This gave an additional 0.93 g., m.p. 198–200° (total yield 28%). Crystallization from ethanol gave fine yellow needles, m.p. 197–197.5°.

Anal. Calcd. for $C_{10}H_{12}O_3N_6$: C, 45.45; H, 4.58; N, 31.81; O, 18.16. Found: C, 45.47; H, 4.61; N, 31.96; O, 18.20.

4-Amino-6-anilino-2-(5-nitro-2-furyl)-1,3,5-triazine (XVIII, R = C_6H_5). 1-Phenyl biguanide[22] (17.70 g., 0.1 mole) and methyl 5-nitro-2-furoate (17.10 g., 0.1 mole) were dissolved in 100 ml. of ethylene glycol monomethyl ether and heated on a steam bath for 3.5 hr. After standing for 3 days at room temperature, the precipitate which had separated was collected and crystallized from dimethylformamide-water. The resulting olive-green product melted at 259.5–260° and weighed 3.18 g. An additional 1.42 g., m.p. 243°, was obtained from the reaction mother liquor (total yield 15.4%). For analysis, the product was crystallized from 1-butanol without change in melting point.

(22) Supplied by the American Cyanamid Co.

Anal. Calcd. for $C_{12}H_{10}N_6O_3$: C, 52.35; H, 3.38; N, 28.18; O, 16.09. Found: C, 52.53; H, 3.50; N, 28.04; O, 16.01.

4-Amino-6-(o-toluidino)-1,3,5-triazine (XVIII, R = *o*-tolyl). A solution of 1-(*o*-tolyl)biguanide[22] (9.55 g., 0.05 mole) and methyl 5-nitro-2-furoate (8.55 g., 0.05 mole) in 30 ml. of ethylene glycol monomethyl ether was allowed to stand at room temperature for 5 days. The yellow product which separated weighed 1.50 g. (9.6%) and melted at 257° dec. Crystallization from 1-butanol did not change the melting point.

Anal. Calcd. for $C_{14}H_{12}O_3N_6$: C, 53.84; H, 3.87; N, 26.91; O, 15.37. Found: C, 53.78; H, 3.74; N, 26.71; O, 15.33.

4-Amino-2-(p-chloroanilino)-6-(5-nitro-2-furyl)-1,3,5-triazine (XVIII, R = *p*-chlorophenyl). A solution of 1-*p*-chlorophenylbiguanide[23] and methyl 5-nitro-2-furoate (15.6 g., 0.0915) in 100 ml. of ethylene glycol monomethyl ether was heated on a steam bath for 2.5 hr. and then allowed to stand at room temperature for 5 days. The orange product was then collected by filtration. This weighed 2.60 g. (8.5%) and melted at 249–249.5°. Crystallization from dimethylformamide-water did not alter the melting point.

Anal. Calcd. for $C_{12}H_9ClN_6O_3$: C, 46.95; H, 2.72; Cl, 10.66. Found: C, 47.13; H, 2.72; Cl, 10.64.

1-(5-Nitro-2-furoyl)-5-(p-nitrophenyl)biguanide (XIX). A solution of methyl 5-nitro-2-furoate (8.55 g., 0.05 mole) and *p*-nitrophenylbiguanide[23] (11.10 g., 0.05 mole) in 200 ml. of ethylene glycol monomethyl ether was allowed to stand at room temperature for 14 days. The yellow solid which deposited during this time weighed 10.69 g. (56%) and melted at 252° dec. Similar results were obtained at room temperature using diethylene glycol dimethyl ether, pyridine, or with refluxing ethanol. Crystallization from acetic acid–ethanol gave material melting with decomposition at 259°. Analysis indicated this material to be a monohydrate; however, attempts to remove the water by drying only resulted in decomposition.

Anal. Calcd. for $C_{12}H_{11}O_8N_7 \cdot H_2O$: C, 41.17; H, 3.45; O, 29.53. Found: C, 41.35; H, 3.35; O, 29.55.

4-Amino-2-(p-nitrophenyl)-6-(5-nitro-2-furyl)-1,3,5-triazine (XVIII, R = *p*-nitrophenyl). *Procedure A.* Compound XIX (6.75 g., 0.0178 mole) was introduced into a few milliliters of boiling dimethylformamide, and the resulting solution immediately cooled in ice. The triazine separated as an olive-green powder, m.p. 338° dec., weighing 0.72 g. Dilution of the mother liquor with water gave 4.35 g. of starting XIX melting at 245° dec. The yield of triazine based on returned starting material was 33% of theory.

Procedure B. A mixture of methyl 5-nitro-2-furoate (8.6 g., 0.05 mole) and 1-*p*-nitrophenylbiguanide (11.1 g., 0.05 mole) in 50 ml. of dimethylformamide was heated for 8.5 hr. on a steam bath. Cooling gave 2.10 g. (12%) of triazine, m.p. 340° dec. If the components were allowed to stand at room temperature for 8 days about 5% of the theoretical amount of the triazine was formed.

For analysis, this triazine was crystallized from dimethylformamide and dried at 150° *in vacuo*, giving material, m.p. 342° dec.

Anal. Calcd. for $C_{13}H_9N_7O_8$: C, 45.25; H, 2.65; N, 28.56. Found: C, 45.25; H, 2.86; N, 28.72.

2,4-Diacetylamino-6-(5-nitro-2-furyl)-1,3,5-triazine (XX). 2,4-Diamino-6-(5-nitro-2-furyl)-1,3,5-triazine[16] (2.22 g., 0.01 mole) was heated under reflux with 50 ml. of acetic anhydride for 1.5 hr. On cooling, 2.22 g. (72.5%) of the diacetyl compound separated, m.p. 269–270° dec. Crystallization from dimethylformamide gave tan colored crystals, m.p. 274.5–275° dec.

Anal. Calcd. for $C_{11}H_{10}O_5N_6$: C, 43.14; H, 3.29. Found: C, 43.06; H, 3.56.

2-Acetylamino-4-amino-6-(5-nitro-2-furyl)-1,3,5-triazine (XVIII, R = $COCH_3$). Hydrolysis of XX in boiling water was attempted; however, its solubility was so low that no

(23) F. H. S. Curd and F. L. Rose, *J. Chem. Soc.*, 362 (1946).

reaction occurred. When XX (2.22 g., 0.00725 mole) was dissolved in a hot mixture of 1:1 dimethylformamide–water and heated under reflux for 16 hr., the monoacetyl compound was obtained on cooling in 1.20 g. yield (63%) of melting at 305° dec. Crystallization from dimethylformamide gave material melting at 317° dec. which was dried at 150° for analysis.

Anal. Calcd. for $C_9H_8N_6O_4$: C, 40.91; H, 3.05; N, 31.81. Found: C, 40.96; H, 3.13; N, 31.73.

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NORTH CHICAGO, ILL.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Synthesis of Polymers Containing Recurring Thiazole Rings

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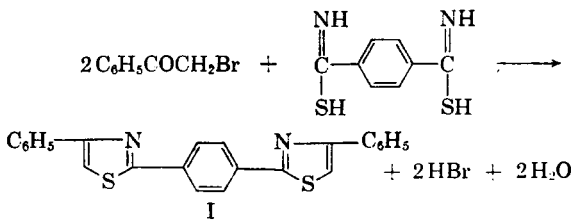
Polymers with molecular weights in the 5000 to 6000 range, one of which is a film-forming material and all of which show fair stability at 300°, have been obtained by condensing *p*-bis(bromoacetyl)benzene with dithioamides.

With the continuing[1] objective of preparing new and thermally stable high molecular weight materials containing aromatic units, a number of new polymers have been synthesized containing benzene rings and thiazole rings in a polymer chain backbone. The thiazole nucleus is more resistant to electrophilic substitutions such as sulfonation[2] than benzene itself.

A preliminary study showed that the model compounds 1,4-bis(4-phenyl-2-thiazolyl)benzene (I) and 1,3-bis(4-phenyl-2-thiazolyl)benzene (II) could be prepared as shown below in good yields by use of refluxing dimethylformamide as a solvent. The condensation of halomethylketones and thioamides has long been known[3] as a general method of preparing thiazoles. Our results encouraged us to believe that similar reactions with bis-α-bromoketones might afford the high yield[4] necessary to produce high molecular weight condensation polymers. Reactions of dithioamides and bis-α-haloketones have been carried out by Erlenmeyer[5] to yield presumably polymeric materials, other than the ones reported here, but the products were not fully characterized.



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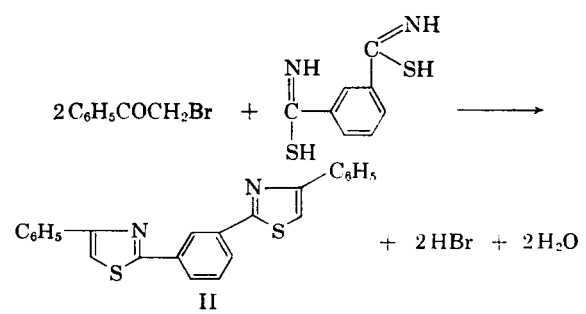
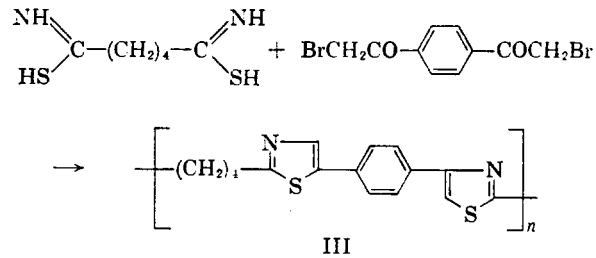


II

Three new thiazole polymers have been prepared and are described below. The dithioamides were made from the corresponding dinitriles by the addition of hydrogen sulfide, and the *p*-bis(bromoacetyl)benzene was prepared by treatment of *p*-diacetylbenzene with bromine in acetic acid.

A polymer (III) was synthesized by condensing dithioaldipamide and *p*-bis(bromoacetyl)benzene in acetic acid as indicated:



III

Polymer III exhibits what appears to be a polyelectrolyte effect in formic acid, displaying inherent viscosities of 3.50, 4.67, and 5.53 at concentrations of 0.239, 0.122, and 0.067 g./100 ml., respectively. However, assuming one bromine atom per chain

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