

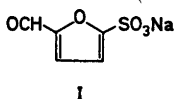
Reactions of 5-Formyl-2-furansulfonic Acid

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Twenty-nine new furan compounds have been prepared from 5-formyl-2-furansulfonic acid sodium salt.

5-Formyl-2-furansulfonic acid sodium salt (I) has recently become easily accessible.¹ It has been used to prepare 29 new furan compounds (II–XXX). Since all reactions employed are well-



known standard reactions, only structures, starting materials, and yields for these new compounds are given (Table 1).

The diversity of the reactions and the generally high yields obtained illustrate that furans with a sulfonyl group in α -position behave as one would expect from the structures in question. No rearrangements or openings of the furan ring, phenomena always to be counted with in furan chemistry, were observed.

The structures of the new furans follow from their syntheses and from elemental analyses. The structure of XI was further proved by the fact that this compound gave no color reaction with iron(III) chloride in aqueous solution.

EXPERIMENTAL

Microanalyses by G. Cornali and W. Egger, Leo Pharmaceutical Products.

5-Formyl-2-furansulfonic acid thiosemicarbazone sodium salt dihydrate (II). I (49.5 g, 0.250 mol) and thiosemicarbazide (22.7 g,

0.250 mol) were dissolved in water (3.6 l). The solution was evaporated from a water bath (80 °C) under reduced pressure. When almost all water had been removed, the residue crystallized. It was dissolved in water (150 ml), and propanol (1 l) was added. The crystalline precipitate formed was isolated by filtration; washing with ether, and drying (70 °C, 15 h). 58.0 g (76 %) of II was obtained as almost white crystals. When heated 2 °C/min in a capillary, the product decomposed with darkening and evolution of gases. When heated rapidly, a clear, colorless gel was formed with evolution of gases around 150 °C. [Found: C 23.6; H 3.5; N 13.6; S 20.6; sulfated ash 23.1. Calc. for $C_6H_8N_3NaO_4S_2 \cdot 2H_2O$ (307.3): C 23.4; H 3.3; N 13.7; S 20.8; ash if Na_2SO_4 23.1]. The compound is sensitive to light.

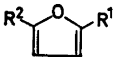
The corresponding anhydrous compound has previously been prepared by Ivanov and Yankov.²

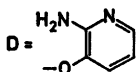
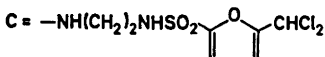
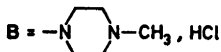
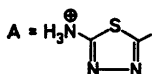
5-Dichloromethyl-2-furansulfonyl chloride (III). To a stirred suspension of I (19.8 g, 0.100 mol) in phosphorus oxychloride (20 ml) was added phosphorus pentachloride (50.0 g, 0.240 mol, Analar BDH) in portions, over a period of about 20 min at 20 °C (cooling). 20 min after the last portion of phosphorus pentachloride had been added, another 19.8 g of I was added in one portion, and again 50.0 g of phosphorus pentachloride was added portionwise at 20 °C over 20 min. These additions were repeated two times more. Thus totals of 79.2 g (0.400 mol) of I and of 200 g (0.960 mol) of phosphorus pentachloride were used. The suspension was stirred at 20 °C for another 90 min. The sodium chloride formed was filtered off and washed with methylene chloride, and the filtrate and washings distilled to give 91.0 g (91 %) of III as a slightly yellow oil, b.p.₁₀ 143–146 °C, n_D^{25} 1.5442. A sample was redistilled and analysed, b.p. 84–85 °C, n_D^{25} 1.5431. [Found: C 24.2; H 1.3; Cl 42.8; S 12.6. Calc. for $C_5H_3Cl_2O_2S$ (249.5): C 24.1; H 1.2; Cl 42.7; S 12.8]. III is a strong vesicant. The product turns dark green on standing.

5-Hydroxymethyl-2-furansulfonic acid sodium salt (IV). I (19.8 g, 0.100 mol), water (50 ml), and wet Raney nickel (4.0 g, BASF H 1–50)

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Table 1. New furan compounds from 5-formyl-2-furansulfonic acid sodium salt.

No.	R ¹		R ²	Prepared from (yield %)
II	SO ₂ Na		CH=NNHCSNH ₂ ·2H ₂ O	I (76)
III	SO ₂ Cl		CHCl ₂	I (91)
IV	SO ₂ Na		CH ₂ OH	I (92)
V	SO ₂ Na		CH ₂ NH ₂	I (75)
VI	SO ₂ -		A	II (62)
VII	SO ₂ NH ₂		CHCl ₂	III (80)
VIII	SO ₂ N(C ₂ H ₅) ₂		CHCl ₂	III (63)
IX	SO ₂ B		CHCl ₂	III (72)
X	SO ₂ C		CHCl ₂	III (94)
XI	SO ₂ D		CHCl ₂	III (76)
XII	SO ₂ Cl		CH ₂ Cl	IV (80)
XIII	SO ₂ -		CH ₂ N+H ₂	V (62)
XIV	SO ₂ Na		CH ₂ NHCOCH ₃	V (50)
XV	SO ₂ NH ₂		CH=NNHCONH ₂	VII (66)
XVI	SO ₂ NH ₂		CH=NNHCSNH ₂	VII (19)
XVII	SO ₂ B		CH=NNHCONH ₂	IX (40)
XVIII	SO ₂ NH ₂		CH ₂ Cl	XII (80)
XIX	SO ₂ N(CH ₃) ₂		CH ₂ Cl	XII (90)
XX	SO ₂ N(C ₂ H ₅) ₂		CH ₂ Cl	XII (58)
XXI	SO ₂ NH ₂		CH ₂ NH ₂ ·HCl	XVIII (77)
XXII	SO ₂ NH ₂		CH ₂ N(CH ₃) ₂ ·HCl	XVIII (51)
XXIII	SO ₂ N(CH ₃) ₂		CH ₂ NH ₂ ·HCl	XIX (71)
XXIV	SO ₂ N(CH ₃) ₂		CH ₂ N(CH ₃) ₂ ·HCl	XIX (74)
XXV	SO ₂ N(NH ₂) ₂		CH ₂ OH	XIX (78)
XXVI	SO ₂ N(C ₂ H ₅) ₂		CH ₂ N(C ₂ H ₅) ₂	XX (62)
XXVII	SO ₂ NH ₂		CH ₂ NHCONHCH ₃	XXI (73)
XXVIII	SO ₂ N(CH ₃) ₂		CH ₂ NHCONHCH ₃	XXIII (92)
XXIX	SO ₂ N(CH ₃) ₂		CH ₂ OCONHCH ₃	XXV (80)
XXX	SO ₂ N(C ₂ H ₅) ₂		CH ₂ N(C ₂ H ₅) ₂ ·HCl	XXVI (46)



were shaken in a glasslined autoclave under hydrogen (50 atm) at about 80 °C. After 2 h of shaking absorption of hydrogen ceased. The catalyst was filtered off, and the filtrate evaporated to dryness (100 °C, 10 mmHg). 18.3 g (92 %) of IV remained as faintly yellow crystals, m.p. about 195 °C (decomp.). [Found:

C 29.9; H 2.6; S 15.5; sulfated ash 35.8. Calc. for C₆H₇NaO₅S (200.2): C 30.0; H 2.5; S 16.0; ash if Na₂SO₄ 35.5].

5-Aminomethyl-2-furansulfonic acid sodium salt (V). I (19.8 g, 0.100 mol), water (35 ml), ammonia (40 ml), and wet Raney nickel (2.4 g, BASF H 1-50) were shaken in a glasslined autoclave under hydrogen (50 atm) at 65 °C for 1 h. The catalyst was filtered off, and the filtrate evaporated to dryness from a water bath (100 °C, 10 mmHg). 20.6 g of crude V remained as white, hygroscopic crystals. The content of V in the crude product was at least 15 g (corresponding to a 75 % yield) as judged by the below transformation of V into XIII. A sample was crystallized from ethanol-water (4:1) and dried (100 °C, 0.1 mmHg). [Found: C 29.0; H 3.5; N 6.1; S 15.1. Calc. for C₆H₇NNaO₅S (199.2): C 30.1; H 3.0; N 7.0; S 16.1. Calc. for C₆H₇NNaO₅S + 3.8 % H₂O: C 29.0; H 3.3.]

2-Amino-5-(2-sulfo-5-furyl)-1,3,4-thiadiazole (VI). II (20.0 g, 0.0650 mol) was dissolved in water (200 ml), and the solution mixed with a solution of iron(III) chloride hexahydrate (47.2 g, 0.172 mol) in water (400 ml). The solu-

tion was heated to 80–90°C for 30 min and then cooled to 0°C. The brown precipitate formed was filtered off and dried, whereby 10.0 g (62 %) of crude VI, m.p. above 300°C, was obtained. Boiling with water (800 ml) and carbon black (1.5 g) followed by hot filtration, and partial evaporation of the filtrate gave 7.70 g of VI as slightly yellow needles, m.p. above 300°C [Found: C 29.1; H 2.2; N 17.1; S 25.8; equivalent weight by acidimetric titration: 251 Calc. for $C_5H_5N_2O_4S_2$ (247.3): C 29.2; H 2.0; N 17.0; S 25.9].

5-Dichloromethyl-2-furansulfonamide (VII). Gaseous ammonia was passed into a stirred solution of III (25.0 g, 0.100 mol) in ether (100 ml) at –30°C, until evolution of heat had ceased. Stirring was continued for another 10 min at 0°C. The ammonium chloride formed was filtered off and washed with ether. The combined filtrate and washings were evaporated to dryness (25°C, 10 mmHg) and the residue crystallized from chloroform (80 ml). 18.5 g (80 %) of VII was obtained as white crystals, m.p. 88–90°C. A sample was crystallized to constant melting point, 90–92°C. [Found: C 25.9; H 2.3; Cl 31.0; N 6.1; S 13.9. Calc. for $C_5H_5Cl_2NO_3S$ (230.1): C 26.1; H 2.2; Cl 30.8; N 6.1; S 13.9].

5-Dichloromethyl-N,N-diethyl-2-furansulfonamide (VIII). VIII was made from diethylamine (2.92 g, 0.0400 mol) and III (5.00 g, 0.0200 mol) in the same way as VII. The resulting, oily residue (5.30 g) was distilled to give 3.61 g (63 %) of VIII as a slightly yellow oil, b.p._{0.3} 140–141°C, n_D^{25} 1.5147. A colorless sample was obtained by another distillation, b.p._{0.05} 122–123°C, n_D^{25} 1.5140. [Found: C 37.9; H 4.4; Cl 24.9; N 4.9; S 11.3. Calc. for $C_9H_{13}Cl_2NO_3S$ (286.2): C 37.8; H 4.6; Cl 24.8; N 4.9; S 11.2].

4-(5-Dichloromethyl-2-furansulfonyl)-1-methylpiperazine (IX) hydrochloride. 1-Methylpiperazine (4.00 g, 0.0400 mol) in dry methanol (10 ml) was added dropwise to a stirred solution of III (10.00 g, 0.0400 mol) in dry methanol (60 ml) at 0 to –10°C. The resulting, thick slurry of IX was heated to 40°C, whereby a yellow solution was obtained. This was allowed to stand for 15 min without further heating. Cooling to –20°C gave a white precipitate of IX, which was filtered off and washed with methanol of –15°C (10 ml) and with ether. 10.0 g (72 %) of IX, m.p. 206°C (decomp.), was obtained. A sample was crystallized from methanol, m.p. 206°C (decomp.). [Found: C 34.5; H 4.3; Cl 30.3; Cl[–] 10.2; N 7.8; S 9.3. Calc. for $C_{10}H_{15}Cl_3N_2O_3S$ (349.7): C 34.4; H 4.3; Cl 30.5; Cl[–] 10.2; N 8.0; S 9.2].

N,N'-Bis(5-dichloromethyl-2-furansulfonyl)ethylenediamine (X). A solution of ethylenediamine (0.900 g, 0.0150 mol) and triethylamine (3.03 g, 0.0300 mol) in dry methanol (10 ml) was added dropwise to a stirred solution of III (7.50 g, 0.0300 mol) in dry methanol (25 ml) at –10°C. The resulting, yellow solution

was kept for 15 min without cooling. Dropwise addition of water (75 ml) with stirring gave a yellow crystalline precipitate of X, which was filtered off and washed twice with water. 6.82 g (94 %) of X, m.p. 146–150°C, was obtained. A sample was crystallized from methanol, m.p. 149–150°C. [Found: C 29.9; H 2.5; Cl 29.0; N 5.5; S 13.4. Calc. for $C_{12}H_{12}Cl_4N_2O_3S$ (486.2): C 29.7; H 2.5; Cl 29.2; N 5.8; S 13.2].

2-Amino-3-(5-dichloromethyl-2-furansulfonyloxy)pyridine (XI). III (15.0 g, 0.0600 mol) in pyridine (15 ml) was added dropwise to a stirred solution of 2-amino-3-pyridinol (5.64 g, 0.0600 mol) in pyridine (60 ml) at 25–30°C. The resulting, brown solution was left standing for 10 min at room temperature, then water (300 ml) was added slowly to give a precipitate of XI. Filtration and washing with water gave 14.7 g (76 %) of XI as yellow crystals, m.p. 107–109°C. A sample was crystallized with carbon black from ethanol-water (1:2) to give white crystals, m.p. 107–109°C. [Found: C 37.2; H 2.7; Cl 22.1; N 8.6; S 10.0. Calc. for $C_{10}H_7Cl_2N_3O_3S$ (323.2): C 37.2; H 2.5; Cl 22.0; N 8.7; S 9.9].

5-Chloromethyl-2-furansulfonylchloride (XII). Finely ground IV (100 g, 0.500 mol) was suspended in phosphorus oxychloride (230 g, 1.50 mol) and methylene chloride (250 ml). Pyridine (59.3 g, 0.750 mol) was added dropwise with stirring over a period of about 60 min. The temperature rose to that of the boiling point of the mixture (49°C) and was kept here for another 30 min by external heating. The reaction mixture was cooled to 20°C and poured slowly into water (500 ml) with stirring. The organic phase was separated, dried over sodium sulfate, treated with carbon black (5.0 g), and evaporated from a water bath (60°C, 10 mmHg). The residual black liquid was taken up in boiling methylcyclohexane and the solution treated twice with carbon black. Toluene (65 ml) was added, and the solution was cooled to 0°C, seeded, and left standing for 2 h at –10°C. Filtration and washing with petroleum ether gave 74.0 g (69 %) of XII, m.p. 38–40°C, yellow crystals turning grey overnight, but otherwise stable. [Found: C 28.0; H 1.9; Cl 32.7; S 14.9. Calc. for $C_5H_4Cl_2O_3S$ (215.1): C 27.9; H 1.9; Cl 32.9; S 14.9]. Another 12.0 g (11 %) may be obtained by distillation of the mother liquor (b.p._{0.1} 83°C).

5-Aminomethyl-2-furansulfonic acid (XIII). Crude V (20.6 g) was suspended in water (20 ml) and the pH of the suspension brought to 3 by addition of concentrated hydrochloric acid (about 8 g). The suspension was heated to 100°C and slowly cooled to 0°C. Filtration, washing with water of 0°C (5+3 ml) and ethanol, and drying at 100°C gave 10.9 g (62 %) of XIII as white, slightly hygroscopic crystals. A sample was crystallized from water and dried (100°C, 0.1 mmHg). [Found: C 33.6; H 4.2; N 7.2; S 17.8; equivalent weight by electro-metric titration: 178. Calc. for $C_5H_7NO_3S$

(177.2): C 34.9; H 4.0; N 7.9; S 18.1. Calc. for $C_8H_7NO_4S + 3.7\% H_2O$: C 33.6; H 4.3].

5-Acetamidomethyl-2-furansulfonic acid sodium salt (XIV). V (1.99 g, 0.0100 mol) and acetic anhydride (10 ml) were mixed and heated in a water bath (100°C) for 20 min. The resulting resin was dissolved in 99% ethanol (15 ml) and the solution filtered hot. Evaporation of the filtrate to dryness from a water bath (100°C, 10 mmHg) followed by 3 crystallizations from 99% ethanol (each from 10 ml), and drying (50°C, 0.1 mmHg) gave 1.20 g (50%) of XIV as white, strongly hygroscopic crystals. [Found: C 31.0; H 3.9; N 4.9; S 11.4; sulfated ash 27.1. Calc. for $C_7H_8NNaO_5S$ (241.2): C 34.9; H 3.3; N 5.8; S 13.3; ash if Na_2SO_4 29.4. Calc. for $C_7H_8NNaO_5S + 10.6\% H_2O$: C 31.2; H 4.1].

5-Formyl-2-furansulfonamide semicarbazone (XV). VII (6.90 g, 0.0300 mol), semicarbazide hydrochloride (3.35 g, 0.0300 mol) and sodium acetate (7.38 g, 0.0900 mol) were stirred with water (50 ml) at 35°C for 20 min. Suspended VII was slowly dissolved, and a new precipitate of XV was formed. Cooling to 0°C, filtration, and washing with water, ethanol, and ether gave 4.60 g (66%) of XV as slightly yellow crystals, m.p. 233°C (decomp.). Crystallization from water (150 ml) with carbon black gave 2.91 g of white crystals, m.p. 235°C (decomp.). [Found: C 30.8; H 3.5; N 23.7; S 13.9. Calc. for $C_8H_8N_4O_4S$ (232.2): C 31.0; H 3.5; N 24.1; S 13.8].

5-Formyl-2-furansulfonamide thiosemicarbazone (XVI). VII (69.0 g, 0.300 mol), thiosemicarbazide (27.3 g, 0.300 mol), and sodium acetate (49.2 g, 0.600 mol) were stirred with water (2 liter) at 50°C for 3.5 h. Cooling to 20°C and filtration gave a semisolid precipitate, which was crystallized from water (4 l) with carbon black. 14.2 g (19%) of XVI was hereby obtained as yellow crystals, m.p. about 240°C. A sample was recrystallized, m.p. 242°C (decomp.). [Found: C 28.9; H 3.3; N 22.2; S 25.6. Calc. for $C_8H_8N_4O_3S_2$ (248.3): C 29.0; H 3.3; N 22.6; S 25.8].

4-(5-Formyl-2-furansulfonyl)-1-methylpiperazine semicarbazone hydrochloride (XVII). IX (0.525 g, 0.00150 mol) and semicarbazide hydrochloride (0.167 g, 0.00150 mol) were dissolved in water (5 ml). The solution was left standing (1 h) at room temperature and then evaporated to dryness from a water bath (100°C, 10 mmHg). The white, crystalline residue was crystallized from methanol (10.0 ml, cooling to -15°C); yield 0.210 g of XVII (40%), m.p. 240°C (decomp.). [Found: C 37.3; H 5.3; Cl⁻ 10.2; N 19.6; S 9.1. Calc. for $C_{11}H_{18}ClN_4O_3S$ (351.8): C 37.6; H 5.2; Cl⁻ 10.1; N 19.9; S 9.1].

5-Chloromethyl-2-furansulfonamide (XVIII). Gaseous ammonia (17.0 g, 1.00 mol) was passed into a stirred solution of XII (97.0 g, 0.450 mol) in ether (600 ml) at 10°C over a period of about 100 min. Stirring was continued for another 60 min at 20°C. The ammonium chloride formed

was filtered off. The filtrate was evaporated to dryness (60°C, 10 mmHg) and the residue crystallized from chloroform. 70.0 g (80%) of XVIII was obtained as white crystals, m.p. 90–92°C. A sample was recrystallized, m.p. 90–92°C. [Found: C 30.5; H 3.1; Cl 18.5; N 7.0; S 16.3. Calc. for $C_5H_6ClNO_3S$ (195.6): C 30.7; H 3.1; Cl 18.1; N 7.2; S 16.4].

5-Chloromethyl-N,N-dimethyl-2-furansulfonamide (XIX). Dimethylamine (36.0 g, 0.800 mol) in ether (400 ml) was added to a stirred solution of XII (86.0 g, 0.400 mol) in ether (400 ml) at 20°C over a period of about 30 min. The resulting suspension was stirred for another 60 min and filtered. The filtrate was extracted with 0.5% hydrochloric acid (100 ml), dried over sodium sulfate, and evaporated to dryness (60°C, 10 mm). Crystallization of the residual oil from carbon tetrachloride (150 ml) gave 80.0 g (90%) of XIX as white crystals, m.p. 55–57°C. A sample was recrystallized, m.p. 56–57°C. [Found: C 37.4; H 4.5; Cl 16.1; N 6.1; S 14.6. Calc. for $C_7H_{10}ClNO_3S$ (223.7): C 37.6; H 4.5; Cl 15.9; N 6.3; S 14.3].

5-Chloromethyl-N,N-diethyl-2-furansulfonamide (XX). XX was made from diethylamine (16.4 g, 0.225 mol) and XII (24.0 g, 0.112 mol) in the same way as XIX. The crude product was distilled twice, whereby 16.2 g (58%) of XX was obtained as a slightly yellow oil, b.p._{0.1} 120–123°C, n_D^{25} 1.5080. [Found: C 43.0; H 5.7; Cl 14.3; N 5.5; S 12.6. Calc. for $C_9H_{14}ClNO_3S$ (251.7): C 43.0; H 5.6; Cl 14.1; N 5.6; S 12.7].

5-Aminomethyl-2-furansulfonamide hydrochloride (XXI). Sodium azide (3.25 g, 0.0500 mol) was added to a stirred solution of XVIII (9.78 g, 0.0500 mol) in dimethylformamide (100 ml) at 20°C. Stirring was continued for 2 h and the sodium chloride formed filtered off. 5% palladium on carbon catalyst (1.00 g) was suspended in the filtrate, and a solution of hydrazine hydrate (1.37 g, 0.0275 mol) in dimethylformamide (10 ml) was added dropwise with stirring at 20°C over a period of 100 min. When the evolution of nitrogen had ceased [yield 1800 ml (100%)], the catalyst was filtered off and the filtrate evaporated from a water bath (90°C, 10 mmHg). The residue was taken up in water (10 ml), and the solution was adjusted to pH 1 with 3 N hydrochloric acid (17 ml). Removal of a small amount of impurity by filtration, evaporation of the solvent, and crystallization of the residue from ethanol (75 ml) and ether (50 ml) gave 8.20 g (77%) of XXI as greyish crystals, m.p. 170–172°C. A sample was recrystallized, m.p. 173–174°C. [Found: C 28.2; H 4.3; Cl 16.6; N 13.1; S 15.0. Calc. for $C_5H_9ClN_2O_3S$ (212.7): C 28.4; H 4.2; Cl 16.6; N 13.1; S 15.0].

5-Dimethylaminomethyl-2-furansulfonamide hydrochloride (XXII). XVIII (9.80 g, 0.0500 mol) was dissolved in ether (50 ml) and the solution added to a stirred solution of dimethylamine (6.80 g, 0.150 mol) in ether (50 ml) at

0–10 °C over a period of about 90 min. Stirring was continued for another 15 min. Water (10 ml) was added to the resulting, thick suspension. The ethereal phase was separated and the aqueous phase extracted with chloroform (six 100 ml portions). The combined ether and chloroform phases were evaporated to dryness and the residue dissolved in 3 N hydrochloric acid (15 ml). Evaporation to dryness and crystallization of the residue from ethanol (100 ml) gave 6.20 g (51 %) of XXII as greyish crystals, m.p. 190–193 °C. A sample was recrystallized, m.p. 192–194 °C. [Found: C 34.8; H 5.5; Cl 14.9; N 11.4; S 13.4. Calc. for $C_7H_{13}ClN_2O_3S$ (240.7): C 34.9; H 5.4; Cl 14.7; N 11.6; S 13.3]. From the above aqueous phase 0.50 g (5 %) of dimethyl di(5-sulfamoylfurfuryl)ammonium chloride precipitated by scratching, m.p. 209–211 °C. [Found: C 36.1; H 4.7; Cl 8.9; N 10.4; S 15.9. Calc. for $C_{12}H_{18}ClN_2O_6S_2$ (399.9): C 36.1; H 4.5; Cl 8.9; N 10.5; S 16.0].

5-Aminomethyl-2-furansulfonic acid dimethylamide hydrochloride (XXIII). XXIII was prepared from XIX (22.4 g, 0.100 mol) in the same way as XXI. The crude compound was dissolved in ethanol (100 ml) containing hydrogen chloride (3.65 g, 0.100 mol), and a solid impurity was removed by filtration. Addition of ether (200 ml) and filtration gave 17.0 g (71 %) of XXIII, m.p. 145–146 °C. Another crystallization gave white, strongly hygroscopic crystals, m.p. 146–148 °C. [Found: C 34.7; H 5.9; Cl 14.5; N 11.2; S 13.4. Calc. for $C_7H_{13}ClN_2O_3S$ (240.7): C 34.9; H 5.4; Cl 14.7; N 11.6; S 13.3].

5-Dimethylaminomethyl-2-furansulfonic acid dimethylamide hydrochloride (XXIV). Dimethylamine (6.80 g, 0.150 mol) and XIX (11.20 g, 0.0500 mol) in ether (100 ml) were left standing at room temperature for 4 days. Water (15 ml) was added in order to dissolve the precipitate of dimethylamine hydrochloride formed. The ethereal phase was separated, washed with water (three 10 ml portions), and evaporated to dryness. The remaining oil was dissolved in 3 N hydrochloric acid (20 ml) and the solution extracted with ether (50 ml). Evaporation of the aqueous phase to dryness and crystallization of the residue from ethanol (50 ml) gave 10.0 g (74 %) of XXIV, m.p. 174–176 °C. A sample was recrystallized, m.p. 174–176 °C. [Found: C 40.3; H 6.4; Cl 13.4; N 10.2; S 12.0. Calc. for $C_9H_{17}ClN_2O_3S$ (268.8): C 40.2; H 6.4; Cl 13.2; N 10.4; S 11.9].

5-Hydroxymethyl-2-furansulfonic acid dimethylamide (XXV). XIX (22.4 g, 0.100 mol) and potassium acetate (9.80 g, 0.100 mol) were heated under reflux in ethanol (100 ml) for 20 h. The potassium chloride formed was filtered off, and the filtrate was heated under reflux with water (50 ml) and sodium hydrogen carbonate (8.40 g, 0.100 mol), until the evolution of carbon dioxide ceased (4 h). Evaporation of the reaction mixture, addition of water (20 ml), extraction with chloroform (two 50 ml

portions), and distillation of the chloroform solution gave 16.0 g (78 %) of XXV as a yellow oil, b.p._{0.05} 147–150 °C, n_D^{25} 1.5105. [Found: C 41.0; H 5.5; N 6.8; S 13.7. Calc. for $C_7H_{11}NO_4S$ (205.2): C 41.0; H 5.4; N 6.8; S 15.6].

5-Diethylaminomethyl-2-furansulfonic acid diethylamide (XXVI). XX (3.78 g, 0.0150 mol) was dissolved in diethylamine (15 ml) and the solution left standing at room temperature for 18 h. The diethylamine hydrochloride formed was filtered off and the filtrate evaporated to dryness. The residue was taken up in ether, and the solution was filtered in order to remove a small amount of solid material. Distillation of the filtrate gave 2.70 g (62 %) of XXVI as a yellow oil, b.p._{0.1} 123–124 °C, n_D^{25} 1.4906. [Found: C 54.4; H 8.2; N 9.3; S 11.1. Calc. for $C_{13}H_{24}N_2O_3S$ (288.4): C 54.2; H 8.3; N 9.7; S 11.1].

1-(5-Sulfamoylfurfuryl)-3-methylurea (XXVII). To a stirred suspension of XXI (21.3 g, 0.100 mol) and methyl isocyanate (5.70 g, 0.100 mol) in chloroform (200 ml) was added triethylamine (11.0 g, 0.110 mol) in chloroform (100 ml) over a period of 10 min. Stirring was continued for another 60 min and the precipitate formed filtered off and dried. Triethylamine hydrochloride was removed from the precipitate by trituration with water (50 ml) and filtration. The filter cake was dissolved in 1 N sodium hydroxide and the solution treated twice with carbon black. Addition of 3 N hydrochloric acid (30 ml) and filtration gave 17.0 g (73 %) of XXVII as white crystals, m.p. 168–169 °C. A sample was crystallized from nitromethane, m.p. 168–169 °C. [Found: C 36.2; H 4.8; N 17.8; S 13.7. Calc. for $C_8H_{11}N_3O_4S$ (233.3): C 36.0; H 4.7; N 18.0; S 13.7].

1-(5-Dimethylsulfamoylfurfuryl)-3-methylurea (XXVIII). XXIII (14.0 g, 0.0685 mol) was dissolved in acetone (140 ml). Methyl isocyanate (3.90 g, 0.0685 mol) was added and the solution left standing at room temperature for 1 h. Filtration gave 16.5 g (92 %) of XXVIII as white crystals, m.p. 163 °C. A sample was crystallized from ethanol, m.p. 163 °C. [Found: C 41.5; H 5.8; N 15.9; S 12.3. Calc. for $C_9H_{15}N_3O_4S$ (262.3): C 41.4; H 5.8; N 16.1; S 12.3].

Methylcarbamic acid 5-(dimethylsulfamoyl)furfuryl ester (XXIX). About 2 mg of potassium hydroxide was crushed with a spatula in XXV (10.3 g, 0.0500 mol). Methyl isocyanate (2.85 g, 0.0500 mol) was added at 20 °C with stirring and cooling. Heating of the mixture to 45 °C caused the reaction to start as indicated by an increase in temperature. The temperature was kept at 65 °C, at first by external cooling, for 15 min. Crystallization of the reaction product from toluene (50 ml) with carbon black gave 10.5 g (80 %) of XXIX, m.p. 50–51 °C. A sample was recrystallized from ether, m.p. 52–53 °C. [Found: C 41.1; H 5.4; N 10.5; S 12.3. Calc. for $C_9H_{14}N_2O_5S$ (262.3): C 41.1; H 5.4; N 10.7; S 12.2].

5-Diethylaminomethyl-2-furansulfonic acid di-

ethylamide hydrochloride (XXX). The compound was made from XXVI in the usual way and crystallized from ethanol. Yield 46 % of XXX, m.p. 148 °C. [Found: C 48.0; H 7.7; Cl 10.9; N 8.5; S 10.0. Calc. for $C_{13}H_{25}ClN_2O_3S$ (324.9): C 48.1; H 7.8; Cl 10.9; N 8.6; S 9.9].

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