2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannosyl chloride (*5*). *4* [6,7] (3.3 g) was dissolved in diethyl ether (40 ml) saturated with hydrogen chloride and stirred for 2 h at room temperature. The crude product obtained after evaporation was used in the following step.

Benzyl 3,6-di-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-2,4-di-O-benzyl-α-D-mannopyranoside (*7*). *3* (1.12 g), mercury(II) bromide (1.5 g) and mercury(II) cyanide (1.5 g) were dissolved in toluene–nitromethane (1:1, 300 ml) and *5* (from 3.3 g *4*) was added. The mixture was stirred for 48 h at room temperature when further portions of *5* (from 2.0 g *4*) and mercury(II) cyanide (0.5 g) were added. The stirring was continued for 24 h when chloroform (500 ml) was added. The chloroform phase was washed with solutions of saturated sodium hydrogen carbonate and potassium iodide and finally with water and evaporated to dryness. The products were fractionated on silica gel using toluene–ethyl acetate (3:1) as irrigant to give crude *6* (2.84 g) as a syrup. Crude *6* (166 mg) was dissolved in methanol (50 ml) and a piece of sodium (~20 mg) was added. The mixture was left at room temperature overnight, neutralized with Dowex 50 (H^+) and evaporated to dryness. Compound *7* was isolated as a syrup [93 mg, 49 % from *3*, $[\alpha]_{589}^{22}+58°$ (*c* 0.2, chloroform)] after chromatography on silica gel using toluene–ethyl acetate (2:1) as irrigant. ^{13}C NMR ($CDCl_3$, ref. internal TMS): δ 101.6, 99.8 and 96.3 (anomeric carbons).

3,6-Di-O-(α-D-mannopyranosyl)-D-mannose (*8*). *7* (88 mg) was dissolved in methanol (55 ml) and hydrogenated at 400 kPa over 10 % palladium on charcoal (100 mg). After work-up, *8* was obtained as a syrup [35 mg, 100 %, $[\alpha]_{589}^{22}+59°$ (*c* 0.3, water)]. ^{13}C NMR (D_2O, ref. external TMS): δ 103.7 and 100.8 [^1J (Cl, Hl) = 171 Hz and 170 Hz, Cl of α-D-mannosyl groups], 95.5 [^1J (Cl, Hl) = 170 Hz, Cl of α-D-mannose residue], 95.0 [^1J (Cl, Hl) = 161 Hz, Cl of β-D-mannose residue]. A sample (~5 mg) of *8* was reduced with sodium borohydride and methylated.[11] The methylated alditol showed $T = 0.96$ relative to permethylated cellotriitol on a 3 % OV-1 column at 250 °C and the MS (70 eV) showed, *inter alia*, the following peaks (% rel. int. in brackets and some assignments [9] in square brackets): 88(100), 101(78), 187(42)[aA_2], 219(16)[aA_1], 293(1).

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Preparation of *N*-Sulfonylformamides

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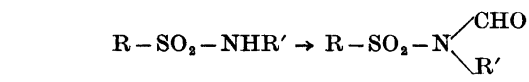
In connection with our investigations of *N*-sulfonylformamidines [1] and *N''*-sulfonylformamidrazones [2] we became interested in the *N*-alkyl- and *N*-aryl-*N*-sulfonylformamides as model compounds in the spectroscopic investigation and as reference compounds for the degradation products. A literature search showed that only the *N*-unsubstituted-*N*-sulfonylformamides had previously been synthesized. As the method described for their preparation [3] did not work for preparation of *N*-substituted-*N*-sulfonylformamides it was necessary to develop new methods. We here report the preparation of *N*-

methyl- and *N*-phenyl-*N*-sulfonylformamides by formylation of the *N*-substituted sulfonamides listed in Scheme 1.



1a – 1d *2a – 2d*

	R	R′
a	*p*-$CH_3C_6H_4$	CH_3
b	CH_3	CH_3
c	*p*-$CH_3C_6H_4$	C_6H_5
d	CH_3	C_6H_5

Scheme 1.

Results. The formylations were carried out in two different ways. The *N*-methylsulfonamides could be formylated by refluxing the amide in anhydrous formic acid. Evaporation of excess formic acid and recrystallization gave the formylated sulfonamides in yields from 52 to 55 %. This method could not be applied to the formylation of *N*-phenylsulfonamides. Even reflux for several days left the sulfonamide unaffected. The formylation of *N*-phenylsulfonamides could, however, be carried out with the mixed anhydride of formic and acetic acid in the presence of sodium acetate. The sulfonamide was dissolved in excess anhydride at room temperature. Anhydrous sodium acetate was added and the mixture was left overnight giving *N*-phenyl-*N*-sulfonylformamides in yields ranging from 71 to 88 %.

The *N*-methylsulfonamides could not be formylated with the mixed anhydride. None of the described methods was adequate for formylation of *N*-unsubstituted sulfonamides as both methods gave lower yields of *N*-sulfonylformamide than the method already published.[3]

Experimental. Microanalyses were carried out in the Microanalysis Department of Chemical Laboratory II, the H. C. Ørsted Institute. ^{1}H NMR spectra were obtained on a JEOL JNM MH 60/II instrument. Mass spectra were taken on an AEI-902 instrument operating at 70 eV. IR spectra were recorded on a Perkin Elmer model 157 NaCl spectrophotometer, only the carbonyl stretching frequency being given. Melting points are uncorrected. All the sulfonamides were prepared by reaction of corresponding amines and sulfonyl chlorides.

Formylation of N-*methylsulfonamides.* The sulfonamide (0.01 mol) was refluxed in anhydrous formic acid (0.5 mol) for 24 h. The reaction mixture was evaporated to dryness and recrystallized from 75 % ethanol.

N-*Methyl*-N-p-*toluenesulfonylformamide*, *2a*. Yield 52 %, m.p. 49 °C. Anal. $C_9H_{11}NO_3S$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 2.45 (3 H, s), 2.95 (3 H, s), 7.15 – 7.73 (4 H, m), 8.97 (1 H, s). IR ($CHCl_3$, cm^{-1}): 1705s. MS *m/e* (% of base peak): 214(1), 213(1)M$^+$, 185(2), 172(3), 155(9), 149(10), 139(2), 121(2), 120(4), 108(100), 91(96).

N-*Methanesulfonyl*-N-*methylformamide*, *2b*. Reflux for 4 h gave 58 % yield, m.p. 72 °C. Anal. $C_3H_7NO_3S$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 3.16 (6 H, s), 8.82 (1 H, s).

IR ($CHCl_3$, cm^{-1}): 1700 s.

MS *m/e* (% of base peak): 138(5), 137(1)M$^+$, 122(8), 109(50), 108(21), 94(32), 80(100), 79(61).

Formylation of N-*phenylsulfonamides.* The sulfonamide (0.1 mol) was stirred for 24 h at room temperature in a mixture of acetic formic anhydride and acetic acid (1:1), (35 ml), chloroform (100 ml) and anhydrous sodium acetate (10 g). The acetic formic anhydride acetic acid mixture was prepared by heating equimolar amounts of anhydrous formic acid and acetic anhydride at 50 °C for 2 h. The chloroform was evaporated, 100 ml of ice water added to the residue and the precipitate was recrystallized from benzene.

N-*Phenyl*-N-p-*toluenesulfonylformamide*, *2c*. Yield 71 %, m.p. 133 °C. Anal. $C_{14}H_{13}NO_3S$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 2.38 (3 H, s), 6.70 – 7.55 (9 H, m). 9.12 (1 H, s).

IR ($CHCl_3$, cm^{-1}): 1710 s.

MS *m/e* (% of base peak): 275(5)M$^+$, 247(5), 211(8), 183(4), 182(5), 168(4), 155(33), 108(18), 91(100).

N-*Methanesulfonyl*-N-*phenylformamide*, *2d*. Yield 88 %, m.p. 124 °C. Anal. $C_8H_9NO_3S$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 3.08 (3 H, s), 7.08 – 7.50 (5 H, m), 8.94 (1 H, s).

IR ($CHCl_3$, cm^{-1}): 1720 s.

MS *m/e* (% of base peak): 199(5)M$^+$, 171(49), 121(2), 119(2), 93(32), 92(100), 77(8).

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