VILSMEIER–HAACK REACTION OF 2-AMINO-X-BENZOTHIAZOLES WITH N-PHENYLFORMAMIDE IN THE PRESENCE OF BENZENESULFONYL CHLORIDE

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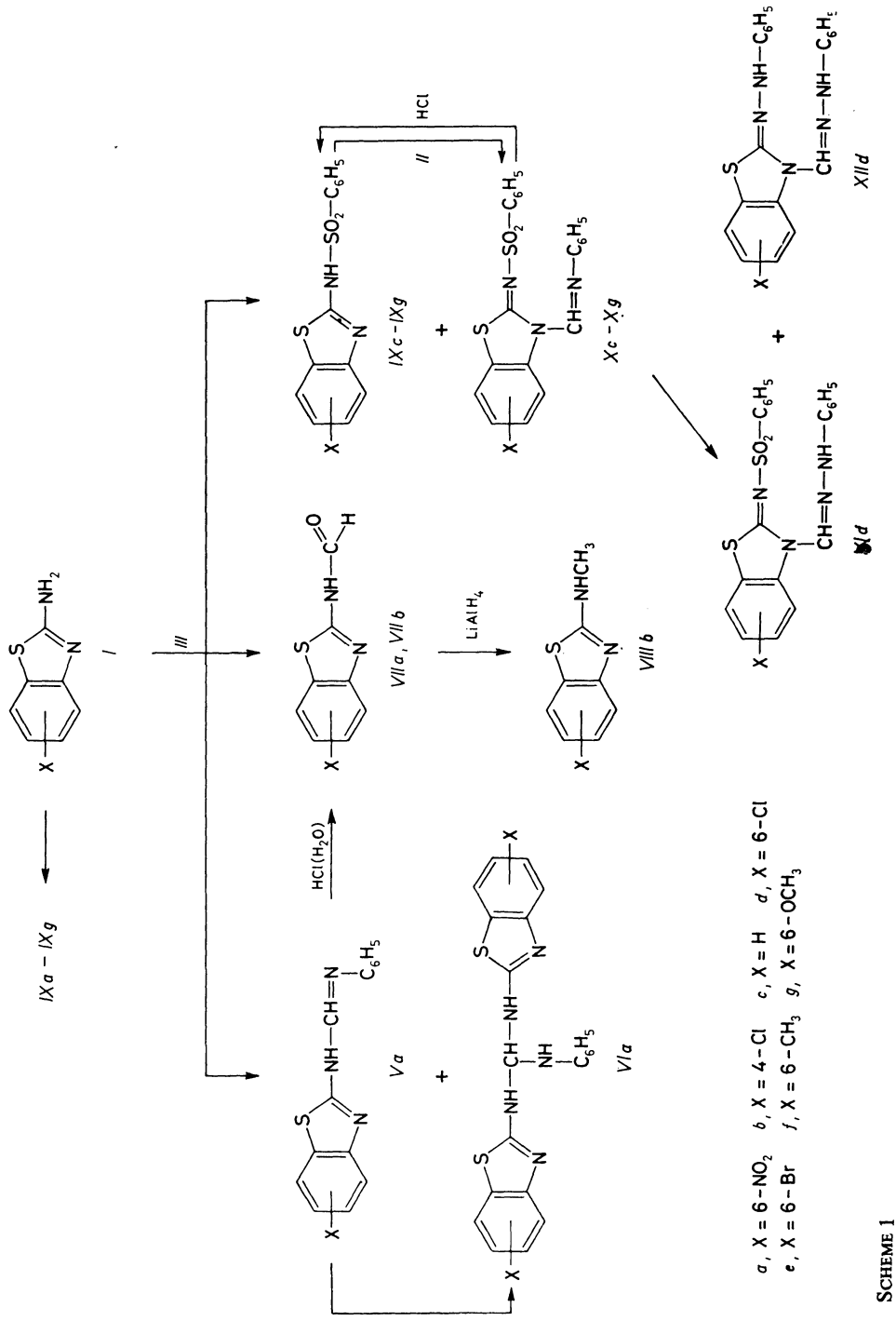
2-Amino-X-benzothiazoles (X = H, 4-Cl, 6-Cl, 6-NO_2, 6-CH_3, 6-OCH_3, 6-Br) react with N-phenylformamide and two equivalents of benzenesulfonyl chloride in pyridine, affording different products in dependence on the substituent X: N-(X-2-benzothiazolyl)formamidines, N-phenyl-N′-(X-2-benzothiazolyl)formamidines, N-phenyl-N′,N″-bis(X-2-benzothiazolyl)triaminomethanes, N-(X-2-benzothiazolyl)benzenesulfonamides and N-2-((X-3-phenyliminomethyl)-benzothiazolylidene)benzenesulfonamides. In the presence of one equivalent of benzenesulfonyl chloride, benzothiazoles *I* either do not react or are partially benzenesulfonated.

Primary[1], secondary[2], and tertiary[3,4] formamides are known to produce with primary amines under conditions of Vilsmeier–Haack reaction the corresponding substituted formamidines. The Vilsmeier–Haack reaction is frequently utilized for synthesizing N,N′,N″-trisubstituted formamidines, since these compounds are formed in very good yields from disubstituted formamides and primary amines in the presence of one equivalent of acid chlorides such as $POCl_3$, $SOCl_2$, $C_6H_5SO_2Cl$ and the like. On the other hand, the reaction of monosubstituted formamides, which is studied also in our work, with primary amines is not so simple, as reactions of the above compounds with the acid chlorides represent preparative reactions for synthesis of the relatively stable intermediate products such as isocyanides[5,6] (yields 50–80%), R-iminofosgenes[7] (RN=CCl_2, yield 98%), dichloroformamidines[8] (RN=CHN(R).$CHCl_2$, yield 80%). Mechanisms of these reactions are not known. It is not known whether the R-iminoformylation activity results from the reaction of the primary formed complexes or from that of some of the relatively stable intermediate products.

The aim of this work was to investigate the reaction of 2-aminobenzothiazole and derivatives thereof (*I*) with the agents $C_6H_5NHC(O)H$–$ClSO_2C_6H_5$ (II) and $C_6H_5NHC(O)H$–$2(ClSO_2C_6H_5)$ (*III*). For this purpose we have chosen 2-aminobenzothiazole and its derivatives substituted on the benzene ring by both electron-acceptor and electron-donor substituents, which allowed to examine substituents effects on the course of the reaction and on formation of reaction products (Scheme 1).

2-Aminobenzothiazole and its derivatives *Ia*–*Ig* belong to weak bases. The basi-


IXa – IXg
I
III
II
HCl
VIIa, VIIb
IXc – IXg
Xc – Xg
LiAlH4
VIIIb
HCl(H2O)
Va
VIa
XIIa – XIIg
a, X = 6-NO2 b, X = 4-Cl c, X = H d, X = 6-Cl
e, X = 6-Br f, X = 6-CH3 g, X = 6-OCH3

SCHEME 1

city of 2-aminobenzothiazole can be compared to that of 2-aminopyridine. Of the compounds *I*, 6-nitro (*Ia*) and 4-chloro (*Ib*) derivatives have the most deactivated amino group. This fact is important since – as follows from studies by Albricht and coworkers[9] and by Lácová and Nguyen thi Nga[10] – the basicity of primary amine effects the direction of the reaction toward either formamidines or benzenesulfonyl derivatives. Benzenesulfonyl chloride (*IV*) has been chosen as the reagent component because it possesses only one bond to chlorine and forms the milder reagent which reflects in the lower complexity of the products.

2-Aminobenzothiazole belongs to the compounds with two centres of nucleophilicity. It is known that alkylations[11] proceed in position 3, while acylations and sulphonations in position 2 on the amino group[12,13]. The reactions with Vilsmeier–Haack reagent so far accomplished[10,14] localize the substituent, similar to acylations, to position 2.

In this study the Vilsmeier–Haack reaction was carried out such that first we have prepared the reagent from $C_6H_5NHC(O)H$ and one or two equivalents of $C_6H_5SO_2Cl$ in pyridine under cooling and than the corresponding substituted 2-aminobenzothiazole was added portionwise to this reagent. The position and type of substituent in the amine *I* affects the reaction course so that under identical conditions different products are isolated (Scheme 1).

In the reaction with 2-aminobenzothiazole derivatives, the complex $C_6H_5NHC.(O)H$–2 $(ClSO_2C_6H_5)$ (*III*) is more efficient compared to the complex $C_6H_5NHC.(O)H$–$ClSO_2C_6H_5$ (*II*). Thus, 2-amino-6-nitrobenzothiazole as the only compound from substrates *I* afforded formamidine derivative with reagent *III* in 20% yield (compound *Va*). The main product was N-phenyl-N',N''-bis(6-nitro-2-benzothiazolyl)-triaminomethane (*VIa*), which is the product of the addition of the unreacted amine *I* to substance *Va*. Compound *VIa* was formed in 92% yield by the reaction of equivalent amounts of *Va* and 6-nitro-2-aminobenzothiazole in pyridine. Compounds *Va* and *VIa* are hydrolysed in 5% hydrochloric acid to give 6-nitro-2-benzothiazolylformamide (*VIIa*).

2-Amino-4-chlorobenzothiazole (*Ib*) gives the only product (84% yield), *i.e.* 4-chloro-2-benzothiazolylformamide (*VIIb*). The increase of the reaction temperature to 80–90°C did not result in change of the product but it led to decrease in its yield (50%). At –5°C we isolated only phenyl isocyanide and the starting substrate *Ib*.

On the basis of the above facts we assume that formamide *VIIb* is formed from a similar intermediate as formamidine *V* but that it suffers further hydrolysis during the isolation process. This leads us to conclude that the formyl group in *VIIb* is located in position 2 on the amino group of the benzothiazole skeleton. This was proved by the reduction of this group to the methyl group by $LiAlH_4$ and by interpretation of ^1H NMR spectra of 4-chloro-2-methylaminobenzothiazole (*VIIIb*). The signal of the methyl group lies at δ 2·66 as the doublet, having interaction

constant $J = 4$ Hz. Formamide *VIIb* is transformylated in the presence of one equivalent of benzenesulfonyl chloride and pyridine with phenylhydrazine to give N-(4-chloro-2-benzothiazolyl)benzenesulfonamide (*IXb*). Amines *Ic–Ig* reacted with reagent *III* to afford two types of the products; the main products were compounds *Xc–Xg* (yields 45–63%) and the side products were substances *IXc–IXg*. To prove that *IXc–IXg* are intermediates for compounds *Xc–Xg*, we have performed the reactions of benzenesulfonamides *IXc–IXg* with *II* in pyridine and obtained nearly quantitative yields of *Xc–Xg*. Theoretically, the phenyliminoformylation can proceed either in position 3 of the benzothiazole moiety or on the nitrogen atom of the sulfonamide group. For sterical reasons we assume that the localization of the phenyliminomethyl group in position 3 of the benzothiazole skeleton is more favorable. This we proved by the reaction of N-(2-(6-chloro-3-phenyliminomethyl)benzothiazolyl)benzenesulfonamide (*Xd*) with two equivalents of phenylhydrazine. We obtained the substitution products, those of substitution of the phenyliminomethyl group and of the benzenesulphonic acid group by phenylhydrazine (compounds *XId* and *XIId*). Both types of the products could be formed only from the presumed structures *Xc–Xg*. The hydrolysis of compounds *Xc–Xg* by dilute hydrochloric acid regenerates benzenesulfonamides *IXc–IXg*.

On the other hand, N-(4-chloro-2-benzothiazolyl)benzenesulfonamide (*IXb*) does not react with reagent *II* in pyridine, eventually it releases benzenesulphonic acid group. In any case, the reaction to position 3 does not take place. From the reaction medium we isolated phenyl isocyanide (50%), the unreacted substrate *IXb* (78%), and 4-chloro-2-aminobenzothiazole (*Ib*) (6%). A similar result has been achieved also when N-(4-chloro-2-benzothiazolyl)-4-methylbenzenesulfonamide was used as the substrate.

Amines *Ia* and *Ib* do not react with reagent *II*, and only phenyl isocyanide and the unreacted substrates *I* are isolated from the reaction mixture. Amines *Ic*, *If*, and *Ig* are benzenesulfonated with reagent *II* (yields 45–50%), and also phenyl isocyanide is isolated in 30–33% yield.

From the experiments described above it follows that the complex $C_6H_5C(O)H$–$ClSO_2C_6H_5$ (*II*), which is suitable for formation of phenyl isocyanide[15], does not loose its benzenesulfonation activity and sulfonates weak bases of the type of 2-aminobenzothiazole (6-methyl and 6-methoxy derivatives) in position 2 in 45–55% yields. As reagent *II* does not react with the deactivated bases such as 4-chloro and 6-nitro derivatives of *I*, which are benzenesulfonated by benzenesulfonyl chloride in pyridine, we do not believe that the benzenesulfonation is caused by the equilibrium mixture of N-phenylformamide and benzenesulfonyl chloride. For weak bases of the type used, complex *II* shows minimal, nearly no phenyliminoformylation activity. Complex $C_6H_5NHC(O)H$–$2(ClSO_2C_6H_5)$ (*III*) is a more reactive Vilsmeier–Haack reagent thant the complex *II*.

EXPERIMENTAL

Infrared spectra were measured on Specord 75 IR (Zeiss, Jena, G.D.R.) in 400—4 000 cm^{-1} region, using paraffine oil. ^1H NMR spectra (in δ scale, ppm) were recorded on Tesla BS 487A (80 MHz) spectrometer, using saturated solutions of the compounds in dimethyl sulfoxide.

N-(6-Nitro-2-benzothiazolyl)-N′-phenylformamidine (*Va*) and
N-Phenyl-N′,N″-bis(6-nitro-2-benzothiazolyl)triaminomethane (*VIa*)

N-Phenylformamide (1 g, 8·2 mmol) and pyridine (10 cm^3) are stirred for 10 min and then benzenesulfonyl chloride (3 g, 17 mmol) is added dropwise at 0—3°C to the stirred solution. The colour of the mixture turns gradually to dark green. The mixture is allowed to react at 60°C for 1 h, cooled and 6-nitro-2-aminobenzothiazole (1·6 g; 7·9 mmol) is portionwise added. After the addition, the reaction mixture is heated while stirred to 60—70°C for 2 h. After pouring onto ice water, the saturated $NaHCO_3$ solution is added, the oily product turns gradually to the yellowish solid which is isolated by filtration with suction, washed with water and dried. The raw product is extracted with benzene (2 × 30 cm^3, 40°C). After partial solvent evaporation, the precipitate formed is recrystallized from benzene–petroleum ether, affording *Va*, m.p. 269—271°C, yield 18%. For $C_{14}H_{10}N_4O_2S$ (298·3) calculated: 56·36% C, 3·37% H, 18·78% N, 10·74% S; found: 56·17% C, 3·12% H, 18·92% N, 10·96% S. ^{1}HNMR spectrum: 7·00—7·50 m, 5 H; 7·62—7·81 t, 2 H; 8·00—8·25 m, 2 H; 8·79 d, 1 H (J = 2 Hz). IR spectrum (in cm^{-1}): ν(NH) 3 180; ν(C=N) 1 630, 1 655; ν(C=C) 1 580; $\nu_s(NO_2)$ 1 329; $\nu_{as}(NO_2)$ 1 501.

The portion insoluble in benzene is recrystallized from dimethyl sulfoxide affording *VIa*, m.p. 343—345°C, yield 50%. For $C_{21}H_{15}N_7O_4S_2$ (491·5) calculated: 51·13% C, 2·66% H, 19·93% N, 13·04% S found: 50·94% C, 2·51% H, 19·68% N, 13·31% S. ^{1}H NMR spectrum 7·28 s, 5 H; 7·62—7·92 t, 4 H; 8·07—8·30 m, 4 H; 8·80 d, 1 H; 8·93 d, 1 H, IR spectrum (in cm^{-1}): ν(NH) 3 110, 3 200, 3 300; ν(C=N) 1 660, 1 635; ν(C=C) 1 590 $\nu_{as}(NO_2)$ 1 514; $\nu_s(NO_2)$ 1 330.

N-(4-Chloro-2-benzothiazolyl)formamide (*VIIb*)

The compound is prepared by the same procedure as *Va* and *VIa*. The raw product is recrystallized from ethanol, m.p. 252—254°C, yield 74%. For $C_8H_5ClN_2OS$ (212·6) calculated: 45·19% C, 2·37% H, 16·67% Cl, 13·17% N, 15·07% S; found: 45·35% C, 2·44% H, 16·31% Cl. 13·29% N, 14·89% S. ^{1}H NMR spectrum: 7·00—7·50 m, 3 H; 7·88 d, 1 H, (J = 8 Hz); 8·58 s, 1 H. IR spectrum (in cm^{-1}): ν(C=O) 1 700; ν(C=N) 1 620; ν(C=C) 1 560; ν(NH) 3 080, 3 185.

Ib: ν(NH) 3 470, 3 280, ν(C=N) 1 615. ^{1}H NMR spectrum: 6·75—7·27 q, 2 H; 7·45—7·60 q, 1 H; 7·70 s, 2 H.

N-(6-Nitro-2-benzothiazolyl)formamide (*VIIa*)

A mixture of *Va* (0·5 g; 1·6 mmol), tetrahydrofuran (10 cm^3), water (10 cm^3), and concentrated hydrochloride acid (10 cm^3) is stirred at 40°C for 1 h. After cooling, the precipitate is isolated by suction, washed and crystallized from toluene, giving *VIIa* melting at 301—303°C in yield 68%. For $C_8H_5N_3O_3S$ (223·2) calculated: 43·04% C, 2·25% H, 18·82% N, 14·36% S; found: 43·28% C, 2·29% H, 18·64% N, 14·16% S. IR spectrum (cm^{-1}): ν(C=O) 1 708; ν(C=C) 1 600, 1 560; $\nu_{as}(NO_2)$ 1 514; $\nu_s(NO_2)$ 1 328; ν(NH) 3 205, 3 088.

4-Chloro-2-methylaminobenzothiazole (*VIIIb*)

VIIb (0·5 g; 2·3 mmol) is dissolved in diethyl ether (20 cm^3) and then $LiAlH_4$ (0·3 g; 7·7 mmol) is added under stirring and cooling. The mixture is heated for 2 h while boiling, cooled, the

precipitate is filtered off and extracted with hot tetrahydrofuran (3 × 20 cm^3). The extracts and filtrate are combined, the solvent is distilled off in vacuo and the residue is crystallized from ether–petroleum ether. *VIIIb* so obtained melts at 129—131°C, yield 90%. For $C_8H_7ClN_2S$ (198·6) calculated: 48·37% C, 3·55% H, 14·10% N, 16·14% S; found: 48·16% C, 3·41% H, 14·18%N, 16 38% S. ^{1}H NMR spectrum: 2 66 d, 3 H, (J = 4 Hz); 6 75—7 62 ., 4 H.

N-(X-3-(Phenyliminomethyl)-2-benzothiazolylidene)benzenesulfonamides *Xc—Xg* and N-(X-2-Benzothiazolyl)benzenesulfonamides *IXc—IXg*

The same procedure was used as in the synthesis of *Va* and *VIa*. The raw product was extracted with boiling ethanol (2 × 10 cm^3). After partial evaporation of the solvent, the ethanol extract is used to isolate products *Xc*, *IXe*, *IXf*, and *IXg* which can be crystallized from ethanol, benzene or their mixture. The portion insoluble in ethanol is crystalized from tetrahydrofuran or benzene, compounds *IXc*, *Xd*, *Xe*, *Xf*, and *Xg* being isolated.

IXc: m.p. 288—289°C, yield 52%. For $C_{13}H_{10}N_2O_2S_2$ (290·3) calculated: 53·78% C, 3·47% H, 9·65% N, 22·08% S; found: 53·48% C, 3·31% H, 9·84% N, 21·89% S. ^{1}H NMR spectrum: 7·00 to 8·06 m, 10 H. IR spectrum (in cm^{-1}): ν(NH) 3 100, 3 170; ν(C═N) 1 609; ν(C═C) 1 560; $\nu_{as}(SO_2)$ 1 320; ν(C—N) 1 308; $\nu_s(SO_2)$ 1 148; $\delta(SO_2)$ 1 090.

IXe: m.p. 274—278°C, yield 12%. For $C_{13}H_9BrN_2O_2S_2$ (369·2) calculated: 42·28% C, 2·45% H 21·63% Br; 7·58% N, 17·36% S; found: 42·46% C, 2·14% H, 21·18% Br, 7·86% N, 17·92% S. ^{1}H NMR spectrum: 7·10—8·25 m, 9 H. IR spectrum (in cm^{-1}): ν(NH) 3 202, 3 050; ν(C═N) 1 664, 1 607; ν(C═C) 1 550, 1 495; $\nu_{as}(SO_2)$ 1 380; ν(C—N) 1 252; $\nu_s(SO_2)$ 1 148, $\delta(SO_2)$ 1 050.

IXf: m.p. 257—258°C, yield 25%. For $C_{14}H_{12}N_2O_2S_2$ (304·4) calculated: 55·24% C, 3·97% H, 9·20% N, 21·06% S; found: 55·39% C, 3·92% H, 9·25% N, 20·78% S. ^{1}H NMR spectrum: 2·30 s, 3 H; 7·37—7·65 m, 5 H; 7·13 s, 2 H; 7·42—8·22 m, 2 H. IR spectrum (in cm^{-1}): ν(NH) 2 990, 2 830; ν(C═N) 1 600; ν(C═C) 1 550; $\nu_{as}(SO_2)$ 1 332; ν(C—N) 1 300; $\nu_s(SO_2)$ 1 150; $\delta(SO_2)$ 1 090.

IXg: m.p. 258—259°C, yield 40%. For $C_{14}H_{12}N_2O_3S_2$ (320·4) calculated: 52·48% C, 3·77% H, 8·74% N, 20·01% S; found: 52·31% C, 3·67% H, 8·76% N, 19·69% S. ^{1}H NMR spectrum: 3·72 s, 3 H; 6·77—7·52 m, 7 H; 7·62—8·22 m, 2 H. IR spectrum (in cm^{-1}): ν(NH) 3 110, 3 168; ν(C═N) 1 604; ν(C═C) 1 550; $\nu_{as}(SO_2)$ 1 322; ν(C—N) 1 302; ν(C—O—C) 1 234; $\nu_s(SO_2)$ 1 151; $\delta(SO_2)$ 1 094.

Xc, m.p. 185—187°C, yield 40%. For $C_{20}H_{15}N_3O_2S_2$ (393·5) calculated: 61·04% C, 3·83% H, 10·67% N, 16·29% S; found: 61·22% C, 3·76% H, 10·48% N, 16·45% S. ^{1}H NMR spectrum: 7·12—8·12 m, 14 H; 8·98 s, 1 H. IR spectrum (in cm^{-1}): ν(C═N) 1 650, 1 590; ν(C═C) 1 500; $\nu_{as}(SO_2)$ 1 340; ν(C—N) 1 312; $\nu_s(SO_2)$ 1 150; $\delta(SO_2)$ 1 089.

Xd, m.p. 294—295°C, yie d 78% For $C_{20}H_{14}ClN_3O_2S_2$ (427·9) calculated: 56·13 C, 3·29% H, 8·28% Cl 9·81% N 14·98% S; found: 56·29% C, 3·23% H, 8·6% Cl, 9·85% N, 15·06% S. ^{1}H NMR (spectrum): 7·00—7·40 m, 5 H; 7·40—7·60 m, 5 H; 7·77—8·20 m, 3H; 8·65—8·85 t, 1 H. IR spectrum (in cm^{-1}): ν(C═N) 1 655, 1 600; ν(C═C) 1 580, 1 530; $\nu_{as}(SO_2)$ 1 338; ν(C—N) 1 309, 1 288; $\nu_s(SO_2)$ 1 155; $\delta(SO_2)$ 1 090. Change of the crystalline structure leads to the substance melting at 215—217°C.

Xe, m.p. 193—196°C, yield 70%. For $C_{20}H_{14}BrN_3O_2S_2$ (472·4) calculated: 50·85% C, ·98% H, 16·81% Br, 8·98% N, 13·57% S; found: 51·13% C, 2·75% H, 16·68% Br, 9·22% N,

13·79% S. ^{1}H NMR spectrum: 7·00—7·40 d, 5 H; 7·4—7·65 m, 5 H; 7·77—8·27 m, 3 H; 8·52 to; 8·87 t, 1 H. IR spectrum (in cm^{-1}): ν(C=N) 1 656, 1 600; ν(C=C) 1 580, 1 530; $\nu_{as}(SO_2)$ 1 340 ν(C—N) 1 309, 1 290; $\nu_s(SO_2)$ 1 154; $\delta(SO_2)$ 1 092.

Xf, m.p. 199—201°C, yield 60%. For $C_{21}H_{17}N_3O_2S_2$ (407·5) calculated: 61·89% C, 4·20% H, 10·31% N, 15·73% S; found: 61·90% C, 4·15% H, 10·34% N, 15·45% S. IR spectrum (in cm^{-1}): ν(C=N) 1 650, 1 600; ν(C=C) 1 585, 1 520; $\nu_{as}(SO_2)$ 1 325; ν(C—N) 1 310, 1 298; $\nu_s(SO_2)$ 1 158; $\delta(SO_2)$ 1 090.

Xg, m.p. 221—223°C, yield 60%. For $C_{21}H_{17}N_3O_3S_2$ (423·5) calculated: 59·55% C, 4·04% H, 9·92% N, 15·14% S; found: 59·49% C, 4·05% H, 10·00% N, 14·91% S. IR spectrum (in cm^{-1}): νC=N) 1 650, 1 610, 1 600; ν(C=C) 1 540; $\nu_{as}(SO_2)$ 1 375; ν(C—N) 1 320; $\nu_s(SO_2)$ 1 155; $\delta(SO_2)$ 1 094.

N-(6-Chloro-3-(phenylhydrazonomethyl)-2-benzothiazolylidene)beznenesulfonamide (*XId*) and 6-Chloro-2-(phenylhydrazono)-3-(phenylhydrazonomethyl)benzothiazoline (*XIId*)

N-(6-Chloro-3-(phenyliminomethyl)-2-benzothiazolylidene)benzenesulfonamide (1 g; 2·3 mmol) is dissolved in dimethylformamide (10 cm^3) and then a solution of phenylhydrazine (0·5 g; 4·6 mmol) in ethanol (15 cm^3) is added dropwise under stirring at 40°C. After 30 min, the mixture is poured into cool water (50 cm^3), mixed, the precipitate is separated, washed twice with water and crystallized from ethanol and again from benzene (compound *XIId*). The ethanol filtrate is precipitated by water and then it is crystallized from tetrahydrofuran (compound *XId*).

XId: m.p. 278—279°C, yield 30%. For $C_{20}H_{15}ClN_4O_2S_2$ (442·9) calculated: 54·18% C, 3·41% H, 12·64% N, 14·47% S; found: 54·41% C, 3·47% H, 12·92% N, 14·15% S. ^{1}H NMR spectrum: 7·12—7·87 m, 14 H; 8·63 s, 1 H.

XIId: m.p. 293—295°C, yield 40%. For $C_{20}H_{16}ClN_5S$ (393·9) calculated: 60·98% C, 4·09% H, 17·78% N, 8·13% S; found: 61·28% C, 4·36% H, 18·03% N, 7·94% S. ^{1}H NMR spectrum: 6·75 to 7·90 m, 14 H; 8·63 s, 1 H; 11·25 s, 1 H.

N-(4-Chloro-2-benzothiazolyl)benzenesulfonamide (*IXb*)

Benzenesulfonyl chloride (4·6 g; 26·1 mmol) is added to a cooled (0—5°C) and stirred solution of 4-chloro-2-aminobenzothiazole (4 g; 21·6 mmol) in pyridine (20 cm^3). After the addition is complete, the mixture is slowly warmed up to 70°C, stirred at this temperature for 2 h, cooled, diluted with ice water (50 cm^3) and neutralized by addition of saturated $NaHCO_3$ solution. After stirring for another 1 h, the precipitate is separated by filtration with suction, washed twice with water, and crystallized after drying from ethanol or an ethanol–tetrahydrofuran mixture, giving *IXb* in 79% yield (5·5 g), m.p. 223—225°C. For $C_{13}H_9ClN_2O_2S_2$ (324·8) calculated: 48·07% C, 2·79% H, 10·92% Cl, 8·62% N, 19·74% S; found: 47·88% C, 2·54% H, 11·04% Cl, 8·64% N, 19·79% S. ^{1}H NMR spectrum: 7·00—7·70 m, 7 H; 7·75—8·00 q, 2 H.

N-(4-Chloro-2-benzothiazolyl)-4-toluenesulfonamide

The compound is prepared by the same procedure as *IXd*, yield 81%, m.p. 188—192°C tetrahydrofuran–ethanol). For $C_{14}H_{11}ClN_2O_2S_2$ (338·8) calculated: 49·62% C, 3·21% H, 10·46% Cl, 8·26% N, 18·92% S; found 49·69% C, 3·15% H, 10·33% Cl, 8·24% N, 18·79% S. ^{1}H NMR spectrum: 2·30 s, 3 H; 7·00—7·85 m, 8 H. IR spectrum (in cm^{-1}): ν(NH) 3 160, 3 133; ν(C=N) 1 600; ν(C=C) 1 546, 1 533; $\nu_{as}(SO_2)$ 1 298; $\nu_s(SO_2)$ 1 138; $\delta(SO_2)$ 1 082.

N-(6-Nitro-2-benzothiazolyl)benzenesulfonamide (*IXa*)

The same procedure is used as for *IXb*, except for the reaction temperature (reflux). The amide is crystallized from dimethylsulfoxide, m.p. 326–328°C (decomp.), yield 85%. For $C_{13}H_9N_3O_4S_2$ (335·3) calculated: 46·5 C, 2·70% H, 12·53% N, 19·12% S; found 46·43% C, 2·69% H, 12·38% N, 19·36% S. IR spectrum (in cm^{-1}): ν(NH) 2 970, 3 100; $\nu_{as}(NO_2)$ 1 545; $\nu_s(NO_2)$ 1 330; ν(C=N) 1 602; ν(C=C) 1 510; $\nu_{as}(SO_2)$ 1 270; $\nu_s(SO_2)$ 1 150.

Reaction of X-2-*aminobenzothiazoles with* $C_6H_5NHC(O)H$–$ClSO_2C_6H_5$ *complex.* A mixture of N-phenylformamide (1 g; 8·2 mmol) and pyridine (10 cm^3) is stirred for 10 min, then benzenesulfonyl chloride (1·5 g; 8·5 mmol) is added dropwise at a temperature of 3–5°C with stirring and the mixture is stirred at 60–70°C for 1 h. Then it is cooled to 0°C and X-2-aminobenzothiazole is added. The mixture is allowed to react at 60–70°C for 2 h, then poured into ice water, saturated $NaHCO_3$ solution is added, the mixture is stirred for another 2 h and the precipitate is separated and crystallized from benzene. The compounds *Ia*, *Ib*, *Ic*, *Ig*, and *If* gave products, substrates *Ia* and *Ib* did not react and were recovered from the reaction mixture unchanged. Substrate *Ic* afforded *IXc*, m.p. 288–289°C, yield 0·8 g (42%). Substrate *If* yielded *IXf*, m.p. 257–258°C, yield 0·9 g (48%). The thiazole *Ig* gave *IXg*, m.p. 258–259°C, yield 0·8 g (45%).

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