Journal of Molecular Catalysis A: Chemical 172 (2001) 165–173

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Reaction of *N*-alkyl-2-benzothiazolesulphenamide with acetic anhydride in the presence of acids
I. Technological aspects

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Received 15 November 2000; accepted 5 March 2001

Abstract

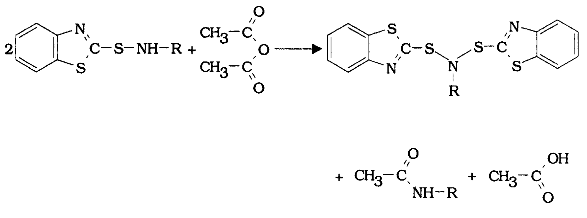
The reaction of *N*-alkyl-2-benzothiazolesulphenamide with acetic anhydride in a non-polar solvent and in the presence of carboxylic or mineral acids at temperatures of 50–90°C has been studied. At low initial concentration of an acid or in its absence a typical autocatalytic behavior of the reaction is observed. However, at higher concentration of acetic acid ($>3\,\mathrm{mol\,dm^{-3}}$), phosphoric or sulphuric acid ($>0.2\,\mathrm{mol\,dm^{-3}}$) the autocatalytic course of the reaction disappeared and higher rate of an *N*-alkyl-2-benzothiazolesulphenamide conversion was observed. The molar ratio of formation of the desired product, alkylbis(2-benzothiazolylsulphen)amide, to the main by-product, alkylamide of acetic acid, is up to 1.6 in the acid catalyzed reaction. The type of alkyl derivatives of 2-benzothiazolesulphenamide has a strong effect on the rate of formation of the corresponding alkylbis(2-benzothiazolylsulphen)amide. The yield of alkylbis(2-benzothiazolylsulphen)amides varies between 80–20 mol% at total conversion of the corresponding sulphenamides in the following order: IPbisBS > CHbisBS > TBbisBS > TAbisBS. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: *N*-alkyl-2-benzothiazolesulphenamides; alkylbis(2-benzothiazolylsulphen)amide; Acetic anhydride; Acid catalysis

1. Introduction

Benzothiazolesulphenamides belong to the class of compounds widely used in the rubber industry as cross-linking agents. Specific properties of these materials have stimulated scientists to study these derivatives in various reactions with potential application in agriculture, pharmacy, as protecting groups in syntheses and in other applications [1,2].

The reaction of *N*-alkyl-2-benzothiazolesulphenamides (alkylBS) with anhydrides of carboxylic acids leads to the formation of corresponding alkylbis(2-benzothiazolylsulphen)amides (alkylbisBS) [3,4]. In the literature is described the use of two types of anhydrides of carboxylic acids. Conly [3] used anhydrides of monocarboxylic acids, e.g. acetic, propionic, butyric acid in the presence or absence of a solvent at 25–75°C (Eq. (1)):



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PII: S1381-1169(01)00141-8

where R represents an alkyl or cycloalkyl radical. In the absence of a solvent, 2–10 mol fold excess of anhydride is required (theoretical molar ratio of alkylBS to anhydride is 2:1). When the reaction is carried out in an inert solvent, e.g. benzene, ethylene chloride, only theoretical molar ratio of the reagents is used. Maison [4] has preferred for the reaction cyclic anhydrides of dicarboxylic acids (maleic, succinic, glutaric acid), anhydrides of aromatic dicarboxylic acids (phthalic, pyromellitic acid), or anhydrides of aromatic monocarboxylic acid (benzoic acid) in the presence of an inert solvent, such as cyclohexane, aliphatic hydrocarbons, carbon tetrachloride, ethylene dichloride. According to Krasuchina et al. [5] the reaction of *N*-cyclohexyl-2-benzothiazolesulphenamide (CHBS) with phthalanhydride is a two step process. In the first step is formed cyclohexylbis(2-benzothiazolylsulphen) amide (CHbisBS) which in the next step produces mainly 2,2′-dithiobisbenzothiazole (MBTS) and *N*,*N*′-dicyclohexylphthalamide. Ignatov et al. [5] synthesized CHbisBS with 78% yield in the presence of butylacetate at 75°C and a molar ratio of CHBS to acetic anhydride 1:100. At the equimolar ratio of the reactants the conversion of CHBS drops from 100 to 70% and the yield of CHbisBS is only about 20%. However, the yield of MBTS increases from 10 to 40%. The main by-products are cyclohexylamide of carboxylic acid and MBTS. In addition, the formation of ArSNH–HNSAr (Ar: benzothiazole) was observed.

In this work, we have studied the technological aspects of an acid catalyzed reaction of various *N*-alkyl-2-benzothiazolesulphenamides with acetic anhydride in a non-polar solvent.

2. Experimental

2.1. Materials

N-isopropyl-2-benzothiazolesulphenamide (IPBS), *N*-*tert*-butyl-2-benzothiazole-sulphenamide (TBBS), *tert*-butylbis(2-benzothiazolylsulphen)amide (TBbis BS) and CHBS, MBTS were commercial products purchased from Monsanto Co., and/or Istrochem Co. (SR). Benzothiazole (BT) was obtained from Aldrich. *N*-*tert*-amyl-2-benzothiazolesulphenamide (TABS), *N*-*tert*-octyl-2-benzothiazolesulphenamide (TOBS) were prepared according to [7]. AlkylBS were purified by crystallization from an ethanol–water solution and alkylbisBS from diethyl ether. The MBTS was purified by washing with acetone. BT was freshly distilled under vacuum. *N*-*tert*-butylacetamide (TBAA) was prepared from *tert*-butylamine (TBA) and acetic anhydride (Ac_2O). The purity of all materials was checked by NMR spectroscopy and high performance liquid chromatography [8]. Acetonitrile was HPLC gradient quality (Merck). Other chemicals were analytical grade purity.

2.2. Apparatus and experimental procedures

The reaction of TBBS with acetic anhydride was studied in 20 cm^3 glass tubes closed by a Teflon screw cap and an elastic septum. The tubes were immersed in a thermostated water bath and vigorously shaken by a laboratory vibrator.

The tubes were filled with 2.3 g TBBS and 4.5 cm^3 *n*-heptane, flushed with nitrogen, closed and heated up to the reaction temperature. After 5 min, a 2.5 cm^3 mixture of acetic anhydride and acetic acid in the molar ratio 1:0/8.5 was injected into the tubes. In some experiments instead of acetic acid, sulfuric or phosphoric acid were added into the mixture in the molar ratio of acetic anhydride and mineral acid 1:0.17/0.68. At defined time the tubes were withdrawn from the bath and immediately 10 cm^3 of cold distilled water was injected into the tube to stop the reaction. The formed suspension of the reaction mixture was filtered off. Both, filtrate and the solid product (dried overnight at 40°C) were analyzed by high performance liquid chromatography.

In some experiments, instead of TBBS, another derivatives of alkylBS (IPBS, TABS, TOBS or CHBS) were used in equimolar amount corresponding to TBBS.

The conversion of the adequate alkylBS and the yield of reaction products were calculated as follows:

$$\text{conversion of alkylBS (\%)} = \frac{\text{moles of alkylBS reacted}}{\text{moles of alkylBS fed}} \times 100$$

$$\text{yield of alkylbisBS or MBTS (\%)} = \frac{2 \times \text{moles of (alkylbisBS or MBTS) produced}}{\text{moles of alkylBS fed}} \times 100$$

$$\text{yield of BT or alkylAA (\%)} = \frac{\text{moles of (BT or alkylAA) produced}}{\text{moles of alkylBS fed}} \times 100$$

where alkylAA is an adequate alkyl derivative of acetamide.

2.3. Analysis

The solid reaction products, alkylBS, alkylbisBS and MBTS containing a part of BT were analyzed by HPLC. The liquid chromatograph (Shimadzu) was equipped with a binary-gradient solvent delivery system LC 10AD, Rheodyne injection valve, UV–VIS photodiode-array detector, SPD M6A, operating in the range 195–670 nm. A Class LC10 software was used for system control, data acquisition and chromatogram integration. Separation of the compounds was performed on a 150 mm × 3.5 mm i.d. glass column filled with Separon SGX C18, 5 μm, (fy Tessek) using acetonitrile and water as the mobile phase under gradient elution.

AlkylAA and BT present in the mother liquor were analyzed after dilution with methanol using HPLC and the refractometric detector RID-10A. The same type of column was employed using methanol:potassium citrate mobile phase under isocratic conditions at ambient temperature.

3. Results and discussion

The course of the reaction of *N*-alkyl-2-benzothiazolesulphenamide with acetic anhydride in the excess of *n*-heptane as a solvent shows a strong effect of acetic acid on the reaction (Figs. 1 and 2). In the absence of acetic acid, the reaction has an induction period of about 30 min. In repeated experiments the induction period is sometimes different what is probably caused by the homogeneity of the system. During this period, the rate of the reaction is low and only about 7 mol% yield of TBbisBS at around 14% conversion of TBBS was obtained. After this period, the reaction rate sharply increases and during 100 min the conversion of TBBS and the yield of TBbisBS reach about 72 and 42%, respectively. The co-product of the reaction, TBAA, is formed in an equimolar amount to TBbisBS. The by-product is MBTS and its yield raises from 5 to 25% after the induction period.

When the initial concentration of acetic acid is 5 mol dm^{-3} the reaction proceeds without an induction period (Fig. 2). The conversion of TBBS sharply increases (after 10 min it is total), however, the yield of the main product, TBbisBS, continuously raises up to 57% during next 60 min. The molar ratio of TBbisBS:TBAA increases up to 1.6:1. An intermediate product of the reaction is MBTS, whose yield after 10 min of reaction is 51% and then continuously

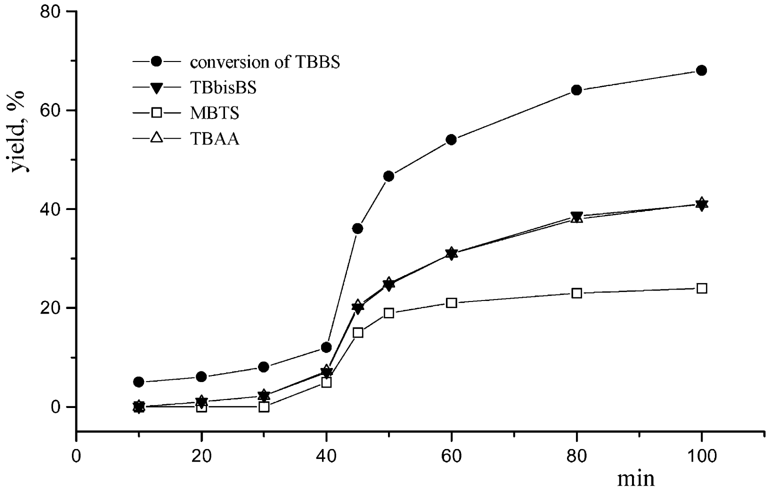


Fig. 1. Time dependence of the products distribution of the reaction of TBBS with acetic anhydride in the absence of initial concentration of an acid at 80°C and [TBBS] = 1.072 mol dm^{-3}, [Ac$_2$O] = 0.58 mol dm^{-3}.

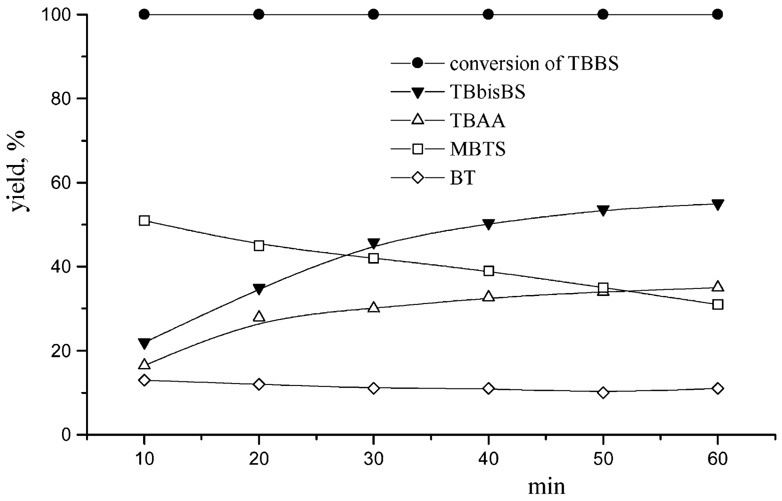


Fig. 2. Reaction of TBBS with acetic anhydride in the presence of acetic acid at 80°C and [TBBS] = 1.072 mol dm^{-3}, [Ac$_2$O] = 0.588 mol dm^{-3}, [AcOH] = 5 mol dm^{-3}.

decreases to 31% after 60 min. As will be shown in the following part of this work, other intermediate products present in the reaction mixture are protonated salt of *N*-acetyl-*N*-*tert*-butyl-2-benzo-thiazolesulphenamide (compound **A**) and protonated salt of *N*-*tert*-butyl-2-benzo-thiazolesulphenamide (compound **B**) which are formed from TBBS (about 16 mol%) by the reaction with Ac$_2$O or H$^+$, respectively. The presence of BT as a by-product is almost constant (about 11% yield) during the reaction.

When the initial concentration of acetic acid is over 3 mol dm^{-3}, the autocatalytic course of the reaction, which is typical for the reaction in the presence of lower concentrations of acetic acid or its absence, disappears (Fig. 3). At lower concentrations of acetic acid (<2 mol dm^{-3}), formation of MBTS and

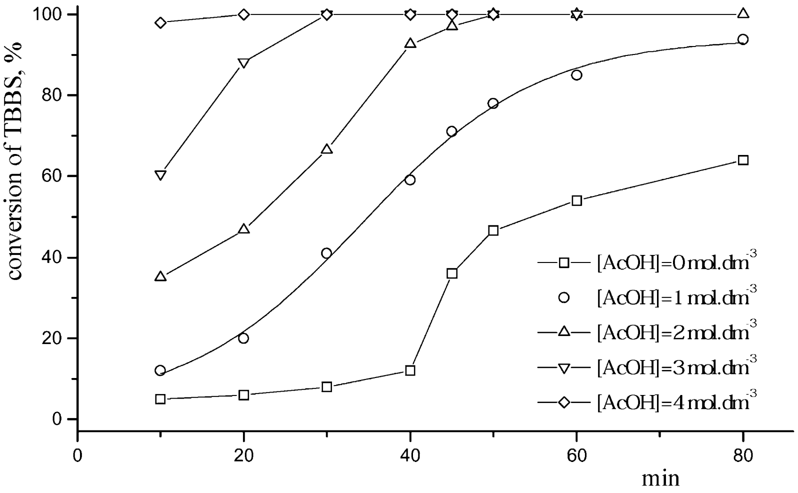


Fig. 3. Effect of acetic acid on the time dependence of the conversion of TBBS at 80°C and [TBBS] = 1.072 mol dm^{-3}, [Ac$_2$O] = 0.58 mol dm^{-3}.

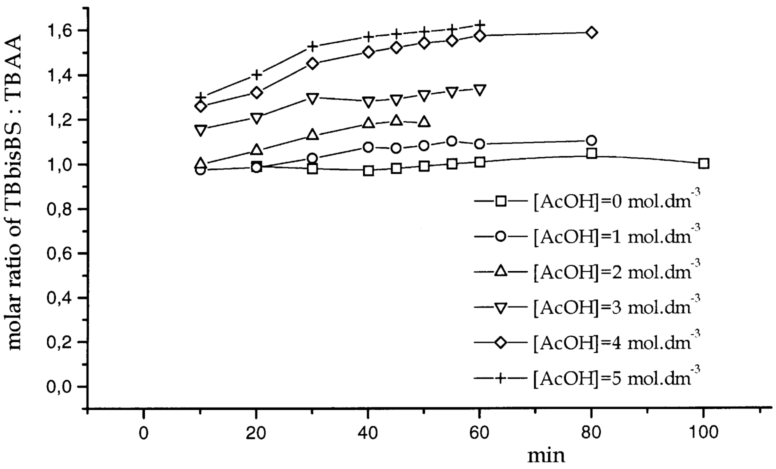


Fig. 4. Effect of acetic acid concentration on the molar ratio of TBbisBS:TBAA at 80°C and [TBBS] = 1.072 mol dm^{-3}, [Ac$_2$O] = 0.58 mol dm^{-3}.

TBbisBS proportionally raises with increasing conversion of TBBS. However, at higher concentrations (>3 mol dm^{-3}) TBBS is during the first 10 min totally converted, mainly to MBTS, the compounds **A** and **B**, partly to BT and unknown aliphatic compounds. With prolongation of the reaction time these compounds are gradually transformed to the desired product (Fig. 2).

At the initial concentration of acetic acid in the reaction system lower than 2 mol dm^{-3}, the formation of TBbisBS and its co-product TBAA is nearly equimolar (Fig. 1). However, with increasing concentration of the acid the molar ratio of TBbisBS:TBAA increases and at a concentration of 5 mol dm^{-3} the ratio reached the value 1.6:1 (Fig. 4).

In Figs. 5 and 6, the influence of strong mineral acids, H$_2$SO$_4$ and H$_3$PO$_4$, on the conversion of TBBS and the yield of TBbisBS is shown. In the presence of both acids at a concentration of 0.1 mol dm^{-3}, the formation of TBbisBS is nearly the same and it increases proportionally with the conversion of TBBS. In the concentration range 0.2–0.4 mol dm^{-3}, the conversion of TBBS is total, however, the yield of TBbisBS is

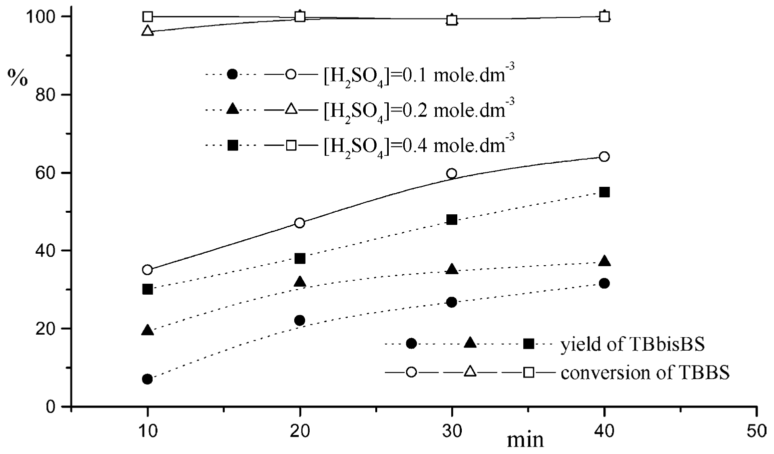


Fig. 5. Effect of H$_2$SO$_4$ concentration on the reaction of TBBS with Ac$_2$O at 80°C and [TBBS] = 1.072 mol dm^{-3}; [Ac$_2$O] = 0.58 mol dm^{-3}.

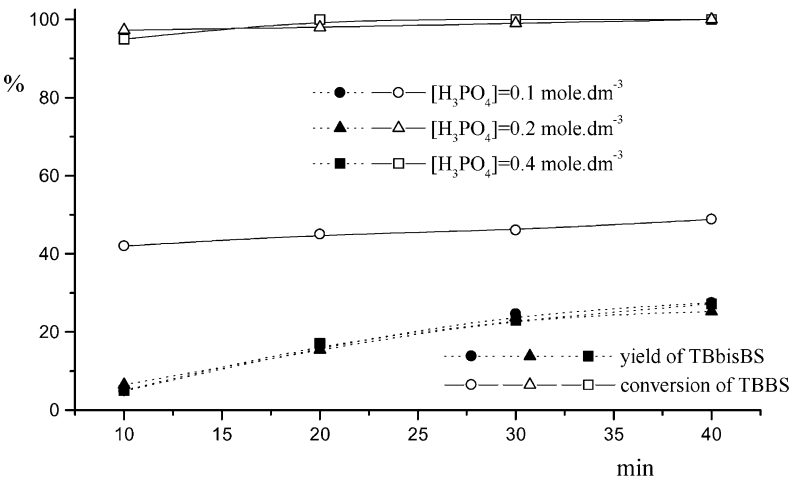


Fig. 6. Effect of H_3PO_4 concentration on the reaction of TBBS with Ac_2O at 80°C and $[TBBS] = 1.072\,mol\,dm^{-3}$; $[Ac_2O] = 0.58\,mol\,dm^{-3}$.

lower in the presence of H_3PO_4 than in the presence of H_2SO_4, practically in the whole concentration range.

The temperature in the range 50–90°C positively influences the rate of formation of TBbisBS (Fig. 7). Also at a temperature 50°C the conversion of TBBS is practically total after 10 min of reaction.

As is shown in Fig. 8, the higher concentration of acetic anhydride increases both, the conversion of TBBS and the yield of TBbisBS. In the same order the formation of MBTS and BT decreases.

The yield of alkylbisBS strongly depends on the type of alkyl derivatives of 2-benzothiazolesulphenamide (Fig. 9). Under studied reaction conditions the conversion of all alkylBS is after 10 min of reaction total. A very high rate of formation and a high yield of alkylbisBS was observed for IPbisBS and CHbisBS, however, the yield of TAbisBS reaches only about 20 mol%. In the absence of acetic acid, this derivative is not produced. Surprising results were obtained with TOBS. In the presence of acetic acid about 30% of

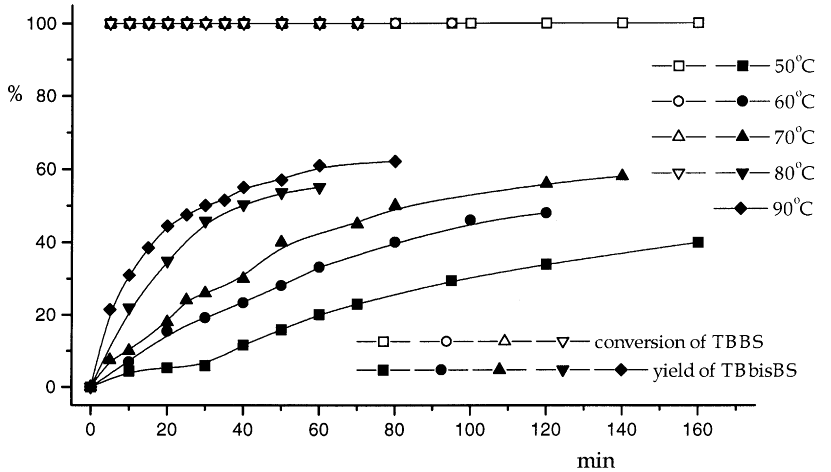


Fig. 7. Effect of temperature on the conversion of TBBS and the yield of TBbisBS at $[TBBS] = 1.072\,mol\,dm^{-3}$; $[Ac_2O] = 0.58\,mol\,dm^{-3}$; $[AcOH] = 4\,mol\,dm^{-3}$.

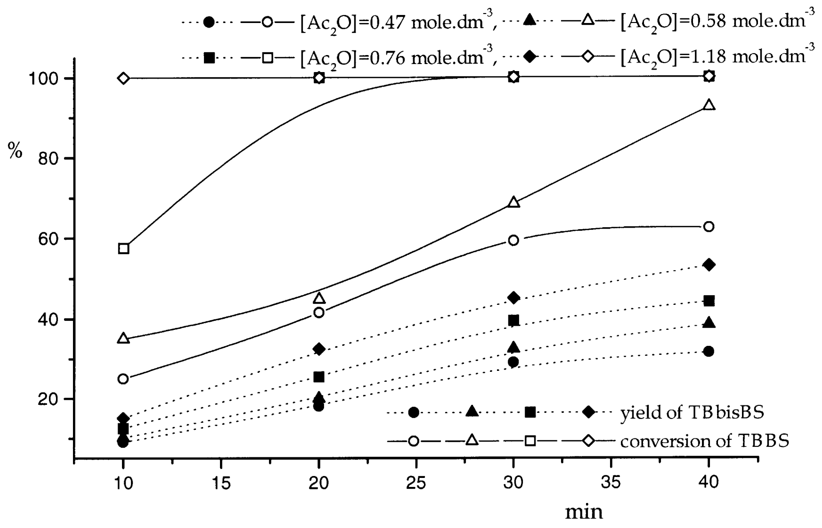


Fig. 8. Effect of concentration of acetic anhydride on the reaction with TBBS at 80°C and [TBBS] = 1.072 mol dm^{-3}; [AcOH] = 2 mol dm^{-3}.

this compound is converted after 60 min, however, the main reaction product is MBTS. The corresponding alkylbisBS and a co-product, an alkylamide of carboxylic acid were not detected in the reaction mixture.

According to the reaction scheme (1), the formation of the desired product, alkylbis(2-benzothiazolylsulphen)amide, is accompanied by the equimolar formation of the corresponding *N*-alkylacetamide. This reaction is catalyzed by an acid, what supports the following facts: (i) increase of the reaction rate with an increase of initial concentration of acetic acid (Fig. 3); (ii) autocatalytic course of the reaction and appearance of the induction period in the absence of acetic acid or at its low initial concentration (<2 mol dm^{-3}); (iii) elimination of the induction period in the presence of strong mineral acids.

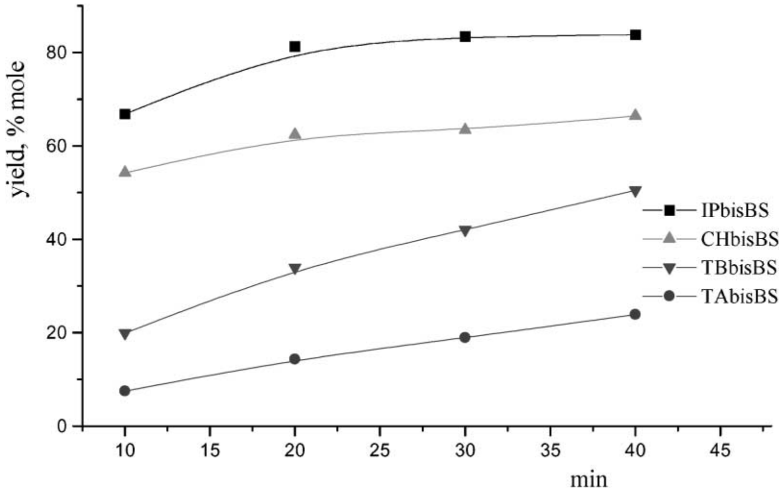
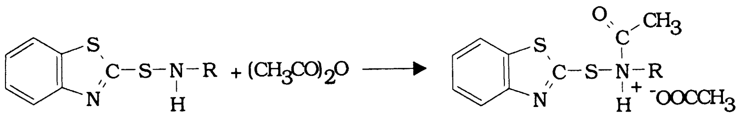


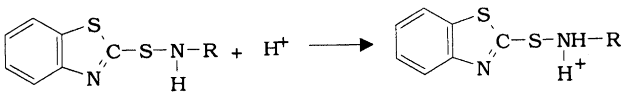
Fig. 9. Effect of various derivative of alkylBS on the yield of alkylbisBS in the reaction with acetic anhydride at 80°C and [alkylBS] = 1.072 mol dm^{-3}; [Ac$_2$O] = 0.588 mol dm^{-3}; [AcOH] = 4 mol dm^{-3}.

Ignatov et al. [6] have proposed that in the first step of the reaction, an *N*-acylated or a protonated salt of alkylBS is formed (Eqs. (2) and (3)). The mentioned compounds in the next step react with another molecule of alkylBS, what leads to the equimolar formation of alkylbisBS and alkylacetamide (Eq. (4)).



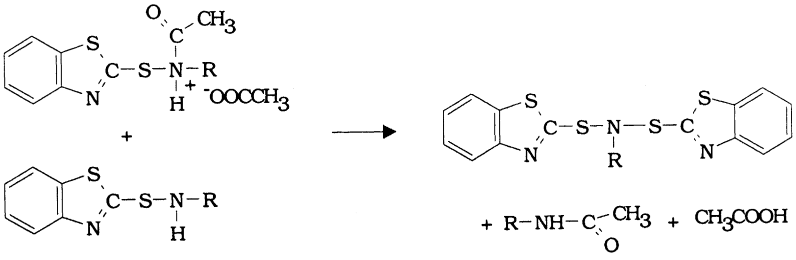
(A)

(2)



(B)

(3)



(4)

We have observed, that at the molar ratio of alkylBS: $Ac_2O = 1:0.5$ and in the presence of a sufficient initial concentration of an acid, the desired bis sulphenamide derivative is formed also after total conversion of alkylBS. At higher concentration of a free acid in the reaction system reaction (3) is preferable. The formed compound **B** probably decomposes without direct formation of alkylbisBS and alkylacetamide. For that reason, the amount of MBTS formed from the aromatic part of the compound **B** by decomposition is high at the beginning of the reaction. The main difference between two pathways of alkylbisBS formation is, that MBTS subsequently reacts with compounds intermediately formed from the aliphatic part of alkylBS what leads to the corresponding alkylbisBS (Fig. 2). Another argument supporting the different pathway of the formation of the desired product is the not equimolar ratio of alkylbisBS to alkylAA, which is for *tert*-butyl derivative of sulphenamide higher than 1.5 (Fig. 4.). If alkylbisBS is formed from compound A and/or compound **B** by reaction with another molecule of alkylBS, the molar ratio of alkylbisBS and alkylacetamide should be theoretically 1:1 (reaction (1)). However, when an alkylbisBS is formed also from intermediately formed MBTS, there is no correlation between the formation of the corresponding alkylacetamide and the desired bissulphenamide derivative.

The length of the alkyl chain (from C_3 to C_8) in the corresponding alkylBS has an important influence on the rate of an alkylbis(2-benzothiazolylsulphen)amide formation (Fig. 9). Using the above described procedure it is not possible to prepare the corresponding alkylbissulphenamide from TOBS. Under the studied reaction conditions TOBS is transformed to MBTS without formation of the alkylbissulphenamide. We suppose that the bulky alkyl group of TOBS sterically hinders the reaction on the nitrogen atom. The less bulky alkyl group in TABS causes that TABS already reacts with Ac_2O to TAbisBS. However, the rate of this reaction is low, the reaction requires a higher initial concentration of an acid and the yield of the formed bissulphenamide derivative is only about 20 mol%. The yields of alkylbisBS of about 80 mol% were obtained only with IPBS under the studied conditions. The order of formation of the corresponding alkylbisBS (yield between 20–80 mol%) is following: TAbisBS < TBbisBS < CHbisBS < IPbisBS.

4. Conclusions

The reaction of an *N*-alkyl-2-benzothiazolesulphenamide with acetic anhydride in the absence and presence of low initial concentrations of an acid has autocatalytic behavior with the induction period. At higher initial concentration of acetic acid (>3 mol dm^{-3}) the autocatalytic course of the reaction disappears and significantly increases the rate of conversion of the corresponding alkylBS. Phosphoric and sulfuric acid have similar effects at concentrations over 0.1 mol dm^{-3}. The reaction of an alkylBS with acetic anhydride is different in the presence and absence of acid catalyst. The acid catalyzed reaction of an alkylBS with Ac_2O leads to the corresponding alkylbisBS and the co-product of the reaction is alkylacetamide. Both products are formed in the molar ratio higher than 1.5, however, in the absence of an acid this ratio is practically equimolar. In an acid catalyzed reaction, the conversion of an alkylBS is practically total after a short time, but the yield of the desired products raises continuously with the duration of the reaction. The differences between acid catalyzed and uncatalyzed reactions are studied more detailed in Part II of this series.

References

[1] L. Craine, M. Raban, Chem. Rev. 89 (1989) 689.
[2] K.A. Petrov, G.V. Rubnev, V.D. Sorokin, Uspechi Chimii. 59 (1990) 1431.
[3] J.C. Conly, US Patent 2,860,142 (1958).
[4] J.M. Maison, France Patent 7,003,351 (1970).
[5] M.M. Krasuchina, I.I. Eitingon, L.V. Andreev, Kauch. Rezina 4 (1974) 23.
[6] V.A. Ignatov, P.A. Akchurina, I.V. Volkov, P.A. Pirogov, Zh. Obshch. Khim. 47 (1977) 1096.
[7] R. Janin, R. Irigny, France Patent 7,235,157 (1972).
[8] M. Štolcová, A. Kaszonyi, T. Liptaj, M. Hronec, J. Chromatogr. A 710 (1995) 351.