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The reaction of benzothiazole sulfenamide with $(TMS)_3SiH$: An example of degenerate-branched chain process

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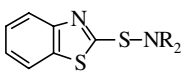
Abstract

The reaction of sulfenamide **3** with $(TMS)_3SiH$ initiated by the decomposition of AIBN at 76 °C has been studied in some detail. The reaction is a rare example of a radical chain-branching process. The two main products are dialkylamine **4** and the thiosilane **5**. It is also established that 2-mercaptobenzothiazole (**2**) is formed in a substantial yield as one of the by-products. The mechanism of this chain autocatalytic reaction is complex due to a mix of different radical chain reactions and some discussion is provided. The amine obtained in a quantitative yield can arise from two independent routes of attack of $(TMS)_3Si^{\bullet}$ radical on sulfenamide **3**. The minor route affords thiol **2** that can act as a catalyst for the major route during the reaction course and then gives a salt with secondary amine, which precipitates upon cooling. The origin of autocatalysis is discussed in some detail.

Keywords: Tris(trimethylsilyl)silane; Sulfenamide; Free radical; Kinetics; Reaction mechanism

1. Introduction

Dialkylaminyl radicals ($R_2N^{\bullet}$) can be generated by a variety of methods [1]. The two main methods that are also compatible with radical chain reactions for synthetic purposes make use of *N*-hydroxypyridine-2-thione carbamates and arenesulfenamides. Newcomb and coworkers [2,3] measured rate constants for a series of dialkylaminyl radical reactions, including cyclizations and hydrogen abstraction from Bu_3SnH, *t*-BuSH, PhSH and PhSeH, using *N*-hydroxypyridine-2-thione carbamates. Tsanaktsidis and coworkers [4,5] reported on the preparation of arenesulfenamides and their utility as precursors of dialkylaminyl radical in the presence of Bu_3SnH. From a variety of arenesulfenamides, the superior reactivity of **1** towards Bu_3Sn radicals was noted. However, in these reactions the presence of small quantities of $(Bu_3Sn)_2O$ significantly improved the reaction performance by increasing the yield of cyclization products. The initial suggestion that this additive catalyzes dialkylaminyl radical reaction [4] was found to be incorrect [3], and later its role was found to be that of scavenging the thiol **2** [3,5], which is a good hydrogen donor and may be produced in situ from the reaction of adventitious disulfide and Bu_3SnH.



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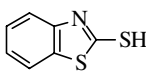

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In the recent years, we have reported two kinetic studies on the reaction of aminyl radicals with $(TMS)_3SiH$. In particular, the hindered 2,2,6,6-tetra-

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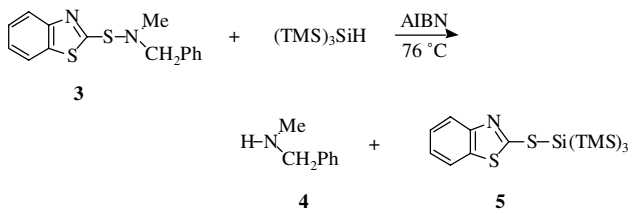
methylpiperidinyl radical [6] and a variety of diarylaminyl radicals [7] were used in connection with some applications of silicon hydrides as process stabilizers for organic polymeric materials subject to oxidative degradation [8]. Since the removal of PhS moiety from a variety of RSPh by $(TMS)_3SiH$ could be an efficient reaction depending on the stabilization of the forming radical R· [8], we tested the reaction of sulfenamide **1** with $(TMS)_3SiH$ in order to verify its potentiality as dialkylaminyl radical precursor. Based on the available kinetic data for the reaction of R_2N· radicals with group 14 hydrides [9,10], we are expecting $(TMS)_3SiH$ to be a relatively good hydrogen donor towards these radicals. We anticipate that the reaction is indeed an efficient chain process producing the corresponding dialkylamine quantitatively and, more importantly, it is a rare example of radical chain-branching process.

2. Results and discussion

2.1. Product studies

Sulfenamide **3** was obtained by the reaction of sulfenyl chloride prepared in situ from the disulfide with the corresponding secondary amine and purified by flash chromatography [4]. When a toluene solution containing equimolar amounts (~0.1 M) of compound **3** and $(TMS)_3SiH$ was heated at 76 °C for 6 h, no new products were formed and the reactants remained unchanged. In the presence of 2,2′-azobisisobutyronitrile (AIBN) as radical initiator, the reaction proceeded smoothly as shown by GC analysis. Scheme 1 shows the formation of the two main products. The yield of amine **4** was nearly quantitative. Product **5** is a new compound, identified by comparison with a sample obtained by an independent synthesis (see below). It is worth mentioning that the GC runs also showed a few minor peaks.

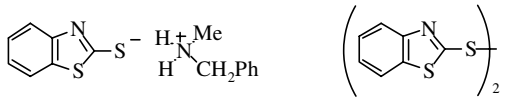
One of these by-products was isolated in a pure form. When the reaction mixtures were left overnight at room temperature after the experiment, lustrous colorless needle-like crystals precipitated in a 5–7% yield with respect to the starting sulfenamide **3**. Chromatographic behavior, NMR, and mass spectrometry analyses indicated



3 4 5

Scheme 1. Product studies showing the quantitative formation of secondary amine **4**.

the compound **6** was formed by the reaction of corresponding amine with thiol. Indeed, this salt could easily be obtained by the addition of an equimolar or somewhat greater amount of amine **4** to a saturated solution of 2-mercaptobenzothiazole (**2**) in toluene. After heating to 90–100 °C followed by cooling to room temperature, lustrous crystals of **6** slowly precipitated.



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Since the early sixties, this reaction has been well known for thiol **2** with a variety of amines, such as piperidine, triethylamine, cyclohexylamine and methylamine [11]. With methylbenzylamine it was never reported. Recently, the salt with $MeNH_2$ has been used in studies of solid-state reactions probed with the atomic force microscope (AFM) [12]. Obtained by us crystals of **6** were soluble in chloroform and less soluble in water. In D_2O, the ^1H NMR spectrum gave an optimal distribution of chemical shifts and integrals for the aromatic protons, whereas in $CDCl_3$ the integrals for each aromatic proton were not well resolved. Chemical shifts of methyl and methylene groups in the salt **6** were distinguishable from those in either the amine **4** or the sulfenamide **3** (see Section 3).

A mixture of 2,2′-dibenzothiazolyl disulfide **7** (as a suspension, 0.43 g) and $(TMS)_3SiH$ (0.32 mL) in toluene (7 mL) was heated for ~7 h at 93 °C in an Ar atmosphere. During this time, the disulfide was completely dissolved to form a transparent weakly yellow solution. The chain reaction, initiated by the decomposition of the disulfide [13], occurred between the components affording the thiosilane **5** and thiol **2** in good yields.

2.2. Reaction mechanism

The effect of the concentration of the initiator and each of the two reactants on the amine formation was investigated one at a time. Fig. 1 shows the influence of the initiation rate (R_i) on the time profile of amine formation using 0.109 M sulfenamide **3** and 0.149 M $(TMS)_3SiH$. AIBN is decomposed at 76 °C with $k_d = 8.15 \times 10^{-5}\ s^{-1}$ and $k_i = 2k_d e = 9.8 \times 10^{-5}\ s^{-1}$, where $e = 0.6$ is the yield of radical escape to the bulk [14]. It can be seen that in all experiments the initial reaction rate (d[**4**]/dt) is much higher than the initiation rate and the reaction kinetics has a pronounced *autocatalytic character*. An increase in R_i increased d[**4**]/dt, and shortened the period of the autocatalytic development of the reaction. Fig. 2 shows that at constant R_i and $[\mathbf{3}]_0$ the reaction rate (d[**4**]/dt) is independent of $(TMS)_3SiH$

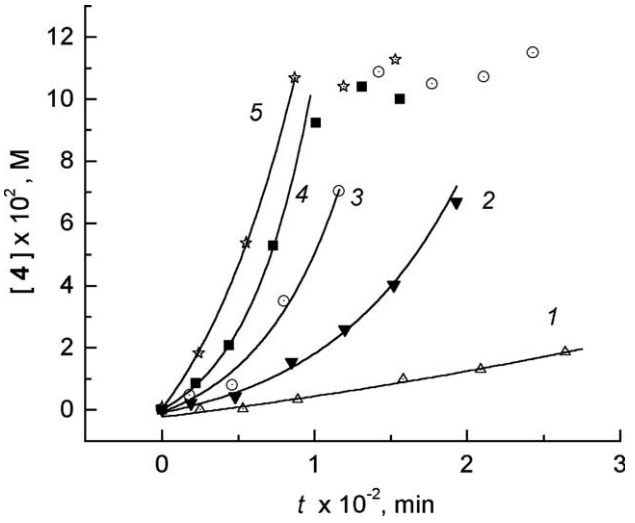


Fig. 1. Influence of the initiation rate (R_i) on the time profile of amine formation. Experiments were carried out in Ar-saturated toluene at 76 °C containing 0.109 M **3** and 0.149 M $(TMS)_3SiH$; curve labels ($R_i \times 10^7$ M s^{-1}): (*1*) 0.59, (*2*) 1.46, (*3*) 2.94, (*4*) 4.45, (*5*) 5.88.

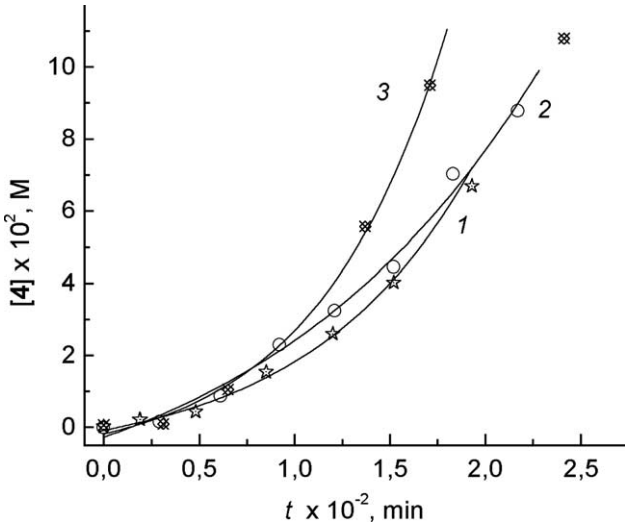


Fig. 2. Influence of the $(TMS)_3SiH$ concentration on the time profile of amine formation. Experiments were carried out in Ar-saturated toluene at 76 °C containing 0.109 M **3** and an initiation rate $R_i = 1.46 \times 10^{-7}$ M s^{-1}; curve labels: (*1*) 0.148 M, (*2*) 0.745 M, (*3*) 1.25 M.

concentration, whereas Fig. 3 shows that at constant R_i and $[(TMS)_3SiH]_0$ the reaction rate (d[**4**]/dt) increased proportionally to the sulfenamide concentration.

The above results suggest that the reaction proceeds via a radical chain mechanism, and that the limiting step involves the sulfenamide **3**. The simplest reaction mechanism that accounts for the two main products is shown in Scheme 2. That is, $(TMS)_3Si^{\bullet}$ radicals, initially generated by small amounts of AIBN, attack the sulfenamide **3** to form product **5** and aminyl radicals by an S_H2-type reaction. Hydrogen abstraction from silane gives the

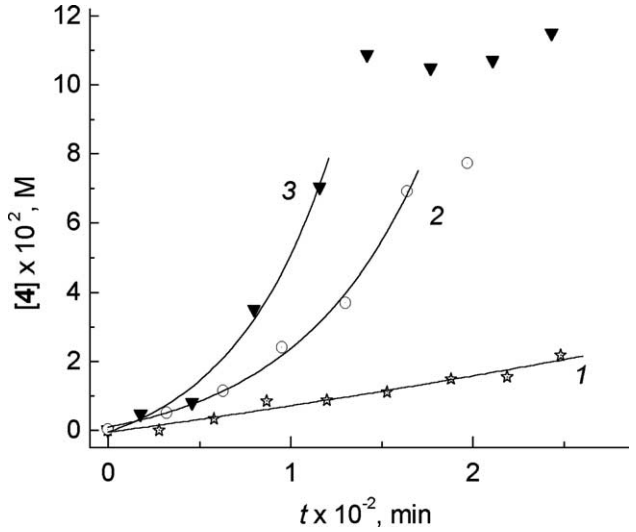


Fig. 3. Influence of the [**3**] on the time profile of amine formation. Experiments were carried out in Ar-saturated toluene at 76 °C containing 0.149 M $(TMS)_3SiH$ and an initiation rate $R_i = 2.94 \times 10^{-7}$ M s^{-1}; curve labels: (*1*) 0.037 M, (*2*) 0.073 M, (*3*) 0.109 M.

Initiation steps

Production of $R^{\bullet}$ at a rate = R_i

$$R^{\bullet} + (TMS)_3SiH \rightarrow RH + (TMS)_3Si^{\bullet} \quad (1)$$

Propagation steps

$$(TMS)_3Si^{\bullet} + \mathbf{3} \rightarrow \mathbf{5} + R_2N^{\bullet} \quad (2)$$

$$R_2N^{\bullet} + (TMS)_3SiH \rightarrow \mathbf{4} + (TMS)_3Si^{\bullet} \quad (3)$$

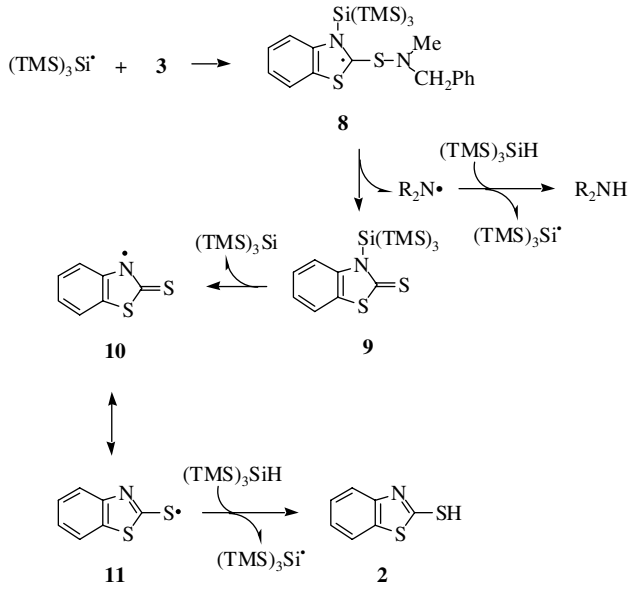
Termination steps

$$2\ (TMS)_3Si^{\bullet} \rightarrow (TMS)_3Si{-}Si(TMS)_3 \quad (4)$$

Scheme 2. Proposed reaction mechanism for the radical initiated reaction of sulfenamide **3** with $(TMS)_3SiH$.

amine **4** and $(TMS)_3Si^{\bullet}$ radical, thus completing the cycle of this chain reaction.

However, the formation of thiol **2** in a 5–7% yield (assuming that all the thiol is transformed to salt **6**) suggests the existence of another path between the reaction of $(TMS)_3Si^{\bullet}$ radical with sulfenamide **3**. We speculate that the attack on the nitrogen atom of benzothiazole moiety to give radical **8** is the most reasonable one (Scheme 3). The addition of silyl radicals to compounds containing C=N bonds is quite extensively described [8,15]. In particular, there are precedents of silyl radical attacking the nitrogen of heteroaromatic rings like substituted pyrimidines and pyrazine, which have been monitored by EPR [16,17]. Radical **8** is expected to decay by β-cleavage of the S–N bond affording the aminyl



Scheme 3. Proposed reaction mechanism for the formation of thiol **2**.

radical and the intermediate **9**. We suggest that this compound is unstable under our experimental conditions and decomposed to give the silyl radical and the aromatic aminyl radical **10**, which is in resonance with form **11**. Indeed, theoretical and spectroscopic data indicated that the unpaired electron is mainly localized on the S atom [18]. Like PhS• radicals under similar conditions [19,20], radical **11** will abstract the H-atom from the silane to give the thiol **2**.

The formation of thiol **2** in mM level during the reaction course can change the nature of one of the propagation steps as reported in Scheme 4 and shows that aminyl radicals abstract hydrogen from the thiol and the resulting thiyl radicals abstract hydrogen from the silane. Hydrogen donor abilities of group 14 hydrides are strongly related to the reaction exothermicities [9]. Based on the rate constants (at 76 °C) of $RCH_2CH_2^{\bullet}$ with Bu_3SnH ($6.1\times10^6\ M^{-1}\ s^{-1}$) and $(TMS)_3SiH$ ($1.2\times10^6\ M^{-1}\ s^{-1}$) and of $R_2N^{\bullet}$ with Bu_3SnH ($1.6\times10^6\ M^{-1}\ s^{-1}$), we estimated a rate constant of $\sim3\times10^5\ M^{-1}\ s^{-1}$ for the reaction of $R_2N^{\bullet}$ with $(TMS)_3SiH$. On the other hand, the reaction of $R_2N^{\bullet}$ with PhSH ($2.8\times10^8\ M^{-1}\ s^{-1}$) is 3 orders of magnitude higher [2] and, therefore, soon after the reaction started,

$$(TMS)_3Si^{\bullet} + \mathbf{3} \rightarrow \mathbf{5} + R_2N^{\bullet} \quad (2)$$

$$R_2N^{\bullet} + \mathbf{2} \rightarrow \mathbf{4} + \mathbf{11} \quad (5)$$

$$\mathbf{11} + (TMS)_3SiH \rightarrow \mathbf{2} + (TMS)_3Si^{\bullet} \quad (6)$$

Scheme 4. Propagation steps for the radical chain reaction of sulfenamide **3** with $(TMS)_3SiH$ in the presence of thiol **2** (cf. Scheme 2).

the propagation step in Scheme 2 will be replaced by the propagation step shown in Scheme 4.

Based on reaction mechanisms in Scheme 2 or 4 and assuming that the reaction (2) is the rate-determining step, the rate of formation of amine is given by Eq. (7).

$$\frac{d[\mathbf{4}]}{dt} = \frac{k_2}{(2k_4)^{1/2}}[\mathbf{3}](R_i)^{1/2}. \quad (7)$$

To determine d[**4**]/dt, the kinetic curves of R_2NH accumulation were approximated by the empirical relation $[R_2NH] = a + be^{ct}$, where a, b and c are the parameters found by the iteration methods. The plots of the initial rates vs. square root of the initiation rate are shown in Fig. 4. This dependence should be fulfilled when the proposed mechanism corresponds to the experimental data. It can be seen that at moderate R_i the experimental points fit satisfactorily the common line. The parameter $k_2/(2k_4)^{1/2} = 4.84\times10^{-2}\ (Ms)^{-1/2}$ obtained from the plot, allows $k_2 = 3.4\times10^3\ M^{-1}\ s^{-1}$ to be calculated at 76 °C by taking $2k_4 = 5\times10^9\ M^{-1}\ s^{-1}$ [8]. Thus, the reaction proceeds via the chain-radical mechanism, although the chains are not too long. For example, using $[\mathbf{3}]_0 = 0.109$, $[(TMS)_3SiH]_0 = 0.149$ M and $[AIBN] = 1.5\times10^{-3}$ M ($R_i = 1.47\times10^{-7}\ M\ s^{-1}$) the initial reaction rate equals only $1.86\times10^{-6}\ M\ s^{-1}$, that is, the chain length is close to 10 units.

Fig. 5 shows how the reaction of **3** with $(TMS)_3SiH$ is inhibited by oxygen. Comparison of curve *2* (on air) with curve *1* (under argon) indicates a considerable decrease in the rate in the presence of O_2. The inhibition effect of O_2 is most likely to be related to the formation of silylperoxyl radicals and their subsequent transformations [21].

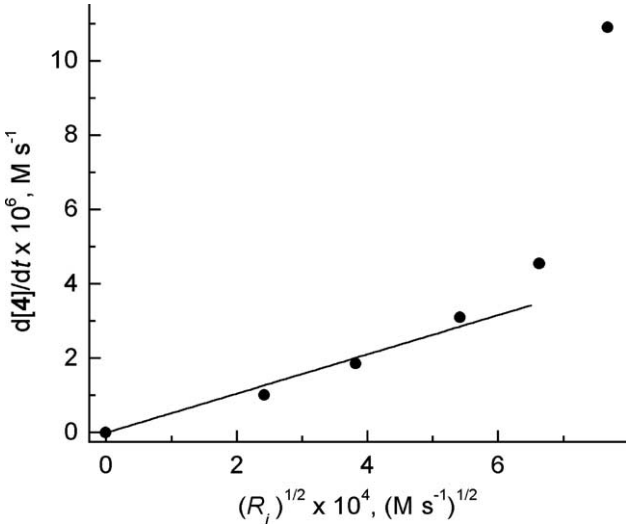


Fig. 4. Plot of the initial rates vs. square root of the initiation rate. Concentrations of reagents: [**3**] = 0.109 M and $[(TMS)_3SiH]$ = 0.149 M.

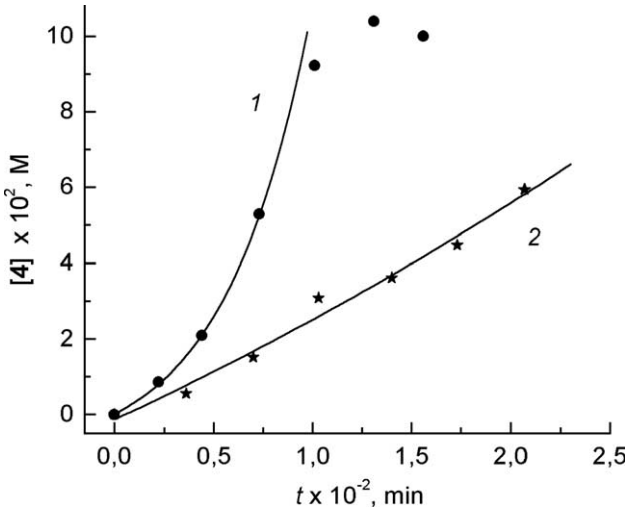


Fig. 5. Influence of oxygen on the kinetics of amine accumulation. $R_i = 4.48 \times 10^{-7}$ M s^{-1}, [**3**] = 0.109 M, and [$(TMS)_3SiH$] = 0.149 M. (*1*) argon, (*2*) air.

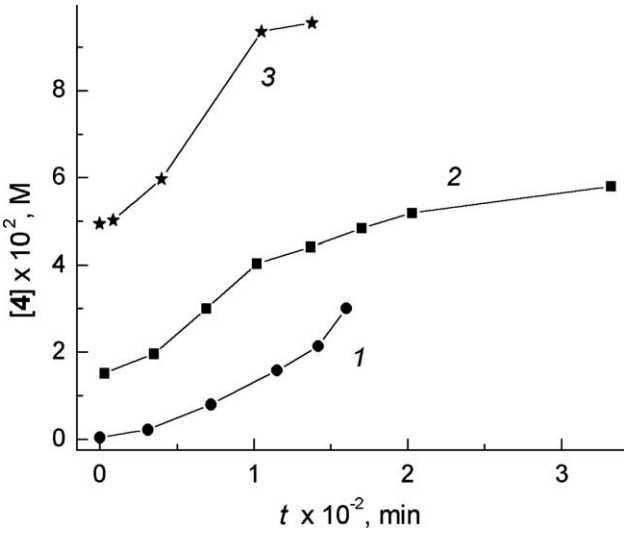


Fig. 6. Kinetic curves of amine formation (*1*) without additives, (*2*) in the presence of 0.0058 M **6**, and (*3*) in the presence of 0.044 M **4**. Experiments were carried out in Ar-saturated toluene at 76 °C containing 0.054 M **3**, 0.163 M $(TMS)_3SiH$ and an initiation rate $R_i = 2.94 \times 10^{-7}$ M s^{-1}.

Finally the reaction of disulfide **7** with $(TMS)_3SiH$ is worth a comment. The reaction is a radical chain process auto-initiated by thermal decomposition of disulfide itself [13]. The propagation steps consist with an S_H2 attack on the sulfur by silyl radical to give the thiosilane **5** and thiyl radical **11**, and hydrogen abstraction from the silane by radical **11**. The reaction of $(TMS)_3Si^{\bullet}$ radical with disulfide **7** is expected to be faster than with sulfenamide **3** and, therefore, the addition to the N of benzothiazole should be less important [22].

2.3. The origin of autocatalysis

According to Scheme 3, additional radical formation is caused by the decomposition of the side product **9**. However, taking into account that thiol **2** is formed in a 5–7% yield and that formation of amine **4** proceeds via chain mechanisms with chain lengths close to 10 units, we can conclude that the highest possible rate of radical formation by radical decomposition of **9** is close to the initiation rate R_i caused by AIBN. Then according to Eq. (7), the rate of the whole process is expected to increase only by a factor of ~1.5, which is too low to explain the experimental findings. Some tests also showed that the main two products **4** and **5** as well as salt **6**, are not responsible for the observed autocatalysis. Fig. 6 shows the reaction kinetics in the presence of small amounts of amine **4** (curve *3*) and salt **6** (curve *2*) and indicates that both compounds have an accelerating effect on the initial rate of the reaction. On the other hand, thiosilane **5** showed high thermal stability that excludes in situ decomposition. We also tested a possible auto-acceleration of the reaction by the acidic catalysis of the radical decomposition of sulfenamide **3** and formation of thiol **2** (as a weak acid), without success [23].

However, we cannot exclude that additional radical formation occurs by reactions involving other products of side processes. One of us has recently studied the radical chain reduction of *N*,*N*′-diphenyl-1,4-benzoquinone-diimine (QDI) by thiol **2** (Eq. (8)) [24].

$$\mathrm{QDI} + 2\ \mathbf{2} \rightarrow \mathrm{QDIH_2} + \mathbf{7} \tag{8}$$

It was found that in the absence of a radical initiator, chain initiation (i.e., formation of free radicals) proceeds via the reaction shown in the following equation.

$$\mathrm{QDI} + \mathbf{2} \rightarrow \mathrm{HQDI}^{\bullet} + \mathbf{11} \tag{9}$$

These findings suggest that autocatalysis in our system can be caused by a similar reaction. Visual observations of the reaction of **3** with $(TMS)_3SiH$ show that the reaction mixtures, colorless in the beginning of experiments, gradually gained a more and more pronounced brownish-orange color. This suggested that compounds with conjugated multiple bonds accumulated during the reaction. We suggest that QDI can be considered as a model of colored by-products of reaction **3** with $(TMS)_3SiH$. Since the concentrations of thiol **2** and colored by-products only increase during the reaction, the rate of radical formation in the reaction between them also increases continuously, and this explains the autocatalytic character of the reaction of **3** with $(TMS)_3SiH$. It is worth also mentioning the observed very strong accelerating effect of amine **4** on the Reaction (8). For example, 3×10^{-3} M **4** increases the initial rate by ~15 and ~30 times for the reaction of 1×10^{-4} M QDI with 5×10^{-4} M **2** and 1×10^{-4} M QDI with 1×10^{-3} M **2**, respectively. These results indicate possible scenarios for the observed auto-acceleration in the reaction of the sulfenamide **3** with $(TMS)_3SiH$.

3. Experimental

3.1. Materials

Commercially available chemicals were purchased from Fluka, Sigma, Aldrich and were used as received. Solvents were purchased from Merck (HPLC grade) and used without further purification. Analytical TLC were carried out on silica gel 60 F_{254} plates (Merck 5744) and revealed with cerium ammonium sulfate/ammonium molybdate reagent. Products were isolated either by fractional crystallization or by flash chromatography on silica gel 60 (Merck, 230–400 mesh). Melting points were determined on a Büchi 510 capillary melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian VXR (^{1}H 400 MHz, ^{13}C 100.6 MHz) spectrometer, using the solvents indicated in parentheses also as the reference peak. $CDCl_3$ signals were at 7.26 and 77.23 ppm, for ^{1}H and ^{13}C NMR spectra, respectively. GC analysis was performed on a HP6850 (Agilent Technologies, Germany) with a flame ionization detector and a HP-5 column ((5% phenyl)-methylpolysiloxane capillary column; 30 m, 0.25 mm i.d., 0.25 μm film thickness). Temperature started from 70 °C, held for 5 min, followed by an increase of 9 °C/min up to 280 °C, held for 10 min. A constant pressure of 13 psi was maintained and nitrogen was the carrier gas. GC/MS spectra were recorded on a HP 5890 (Series II) coupled to a Hewlett–Packard mass selective detector Model 5971A using similar conditions. Helium was the carrier gas. ESI MS spectra were recorded on an Esquire 3000 plus Bruker instrument.

3.2. Synthesis of sulfenamide **3**

The preparation was made according to the literature starting from disulfide (1.3 g; 4 mmol) for the in situ synthesis of sulfenyl chloride and subsequent coupling with *N*-benzylmethyl amine (1 g; 8.2 mmol) [4]. The product was isolated by flash chromatography on silica gel (eluent: *n*-hexane:ethyl acetate 80:20) and in the first fractions it was obtained as a pure product (750 mg; 2.3 mmol; 57% yield). ^{1}H NMR ($CDCl_3$) δ 2.96 (s, 3H, NMe), 4.33 (s, 2H, benzyl CH_2), 7.25–7.48 (m, 7H), 7.84 (d, 1H, J = 7.9 Hz), 7.87 (d, 1H, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$) δ 176.0, 155.1, 137.5, 135.3 (C), 129.1, 128.7, 128.1, 126.1, 123.9, 121.9, 121.2 (CH), 65.2 (CH_2), 45.7 (CH_3). EI MS *m*/*z* 286 (M^+), 165 (100), 122, 77.

3.3. Synthesis of thiosilane **5**

A suspension of 2,2′-dithiobis(benzothiazole) (0.43 g; 1.30 mmol) in toluene (7 mL) was combined with $(TMS)_3SiH$ (0.26 g; 1.03 mmol) and magnetically stirred at 93 °C for 7 h. The reaction was clear after 10 min and GC analysis on the crude reaction mixture showed the formation of thiol and thiosilane. After the starting disulfide was consumed, the reaction mixture was cooled so that thiol crystallized from toluene and was separated by filtration (190 mg; 1.14 mmol; 87%). The filtrate was evaporated and thiosilane **5** was recovered (0.34 g; 0.82 mmol; 63% yield referred to disulfide).

^{1}H NMR ($CDCl_3$) δ 0.27 (s, 27 H, TMS groups), 7.28 (t, 1H, J = 8 Hz), 7.36 (d, 1H, J = 8 Hz), 7.69 (d, 1H, J = 8 Hz), 7.79 (d, 1H, J = 8 Hz). ^{13}C NMR ($CDCl_3$) δ 0.9 (CH_3), 121.0, 121.1, 124.3, 126.8 (CH), 137.6, 153.6, 166.9 (C). EI MS *m*/*z* 412 (M^+), 339 ($M^+ - 73$), 224, 207, 167, 73 (100), 59.

3.4. Synthesis of salt **6**

A solution of thiol **2** (200 mg, 1.20 mmol) in toluene (5 mL) was combined with methylbenzylamine (373 mg; 1.30 mmol) and heated at 90–100 °C for 1 h under nitrogen atmosphere. Upon cooling the reaction mixture at room temperature, crystals were formed and separated by filtration. The salt (288 mg; 1.20 mmol; 83% yield) was washed with cold toluene and dried under vacuum. M.p. 127–128 °C.

^{1}H NMR (D_2O) δ 2.56 (s, 3H, NMe), 4.05 (s, 2H, CH_2), 7.10 (t, J = 6.8 Hz, 1H), 7.22 (t, 1H, J = 7.2 Hz), 7.30–7.36 (m, 5H), 7.40 (d, 1H, J = 8 Hz), 7.52 (d, 1H, J = 8.4 Hz). ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H, NMe), 3.95 (s, 2H, CH_2) 6.59 (broad s, 2H, NH_2), 7.17–7.33 (m, 8H), 7.47 (d, J = 7.6 Hz, aromatic H). ^{13}C NMR ($CDCl_3$) δ –34.1 (CH_3), 54.7 (CH_2), 114.5, 121.1, 123.9, 126.6, 128.2, 129.0, 129.2 (each CH), 132.9, 136.3, 145.5, 189.3 (each C). ESI MS *m*/*z* 288.6 (M^+), 122. $C_{15}H_{16}N_2S_2$ (288.08): Anal. Calc. C, 62.46; H, 5.59; N, 9.71; S, 22.23. Found. C, 62.27; H, 5.57; N, 9.70; S, 22.14%.

4. Summary

The reaction of sulfenamide **3** with $(TMS)_3SiH$ initiated by radicals is an efficient chain process producing the corresponding dialkylamine quantitatively. The reaction mechanism is complex, being also an example of a degenerate-branched chain process. Two parallel reaction mechanisms based on the initial attack of silyl radical on sulfenamide **3** were suggested, one of which affords thiol **2** in a substantial amount. Evidence that additional radical formation in the system derived from the reaction of thiol **2** with the substances containing conjugated multiple bonds formed as by-products, which is also accelerated by main reaction product amine **4**, were also obtained. We believe that these findings can be extended to the reactions of 2-mercaptobenzothiazole sulfenamides with Bu_3SnH and

nicely explain the observed results described in the introduction.

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