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# *A Facile Reaction of Sulphenamide Accelerators with Acetone*

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*N-cyclohexylaminobenzothiazole-2-sulphenamide (CBS) reacts with acetone at ambient temperature to give 2'(benzothiazolylthio) propan-2-one (1), 1, 1-bis-(2'-benzothiazolylthio)-2-cyclohexylaminoprop-1-ene (2), cyclohexylamine, and a trace of 2-mercaptobenzothiazole (MBT). 1 is an intermediate in the production of 2, as it reacts with CBS in the absence of acetone to give 2. 1, 3-bis-(2'-benzothiazolylthio) propan-2-one (3) and 1, 1-bis-(2'-benzothiazolylthio) propan-2-one (4) are also produced in the latter reaction. This reactivity of sulphenamide accelerators should be borne in mind when employing acetone extraction in the analysis of curatives in rubber compounds or vulcanisates.*

Determination of added curatives in compounded but unvulcanised natural rubber normally involves extraction with acetone at ambient temperature[1]. Extraction at higher temperatures is usually avoided because of potential chemical changes in the curatives. In particular, thiuram disulphides are known to undergo decomposition in acetone to give dithiocarbamates[2]. Recently, Jefferson *et al.*[3] observed that tetramethylthiuram disulphide (TMTD) itself reacts slowly with acetone at ambient temperature to give the thiocarbamoyl-thiopropan-2-one (**7**). Presumably, this mode of reaction is also the source of the dithiocarbamates.

During the course of an investigation on the reactions of cyclohexylamine with di-2-benzothiazolyl disulphide (MBTS), two minor products were isolated from a reaction at 50°C in cyclohexane. One of these was identified as 2'-benzothiazolylthiopropan-2-one (**1**). The second was eventually shown to be the enamine (**2**). The other products obtained were *N*-cyclohexylbenzothiazole-2-sulphenamide (CBS), 2-mercaptobenzothiazole (MBT) and the cyclohexylammonium salt (CBM) of MBT. There was also some unreacted MBTS. It was believed that the two unexpected products arose from reaction of either MBTS or CBS with acetone which had been used for the separation of the products. To investigate this further, the reactivity of acetone towards MBTS and CBS was studied.

## MATERIALS AND METHODS

NMR spectra were recorded on a Perkin-Elmer R32 90MHz, a Varian XL200, a Varian VXR-400, or a General Electric QE 300 instrument using tetramethylsilane as the internal standard. I.r. spectra were recorded on a Perkin-Elmer 157 or 377 spectrophotometer. Melting points were obtained on a Mettler hot-stage microscope. The progress of reactions was followed and purity of compounds checked by analytical t.l.c. using Merck silica gel 60 $F_{254}$ pre-coated plates. Merck silica gel 60 (40 – 63 $\mu$m) was used for preparative column chromatography. C, H and N micro-analysis was performed on a Perkin-Elmer 240 instrument. U.v. spectra were recorded on a Pye Unicam SP8-100 spectrophotometer. The solvent was evaporated using a rotary evaporator at reduced pressure (typically 40 mm Hg).

MBTS was recrystallised twice from toluene, melting point (m.p.) 179°C – 179.8°C. CBS was recrystallised from cyclohexane. Acetone, cyclohexane, toluene, ethanol, diethyl ether and petroleum ether were of A.R. grade. The cyclohexylamine was redistilled from $CaH_2$, boiling point (b.p.) 66°C – 68°C at 84 mm Hg.

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**Reaction of MBTS with Cyclohexylamine**

MBTS (665 mg, 2.00 mmol), cyclohexylamine (397 mg, 4.01 mmol) and cyclohexane (4.00 g) were combined in a Carius tube, de-gassed and sealed under vacuum. The tube was shaken at 50°C ± 0.3°C for 160.5 h. The solid was filtered off and washed with cyclohexane. The solvent was evaporated from the filtrate and the residue eluted with dichloromethane on a silica gel column. The principal fraction obtained was CBS (129 mg, 24%), mixed with a small amount of MBTS, and was recrystallised from petroleum ether (b.p. 60°C - 80°C), m.p. 100.4°C - 100.8°C (*Reference 4*, 103°C - 104°C); the i.r. spectrum was identical with the reference spectrum.

Dichloromethane (20 $cm^3$) was added to the solid from the reaction mixture and the mixture heated to boiling. On cooling, the solid (281 mg) was filtered off. By h.p.l.c. analysis [eluting with $MeCN/H_2O$ (70:30) through octadecylsilica gel], this was by weight 59% MBTS, a maximum of 27% of the cyclohexylammonium salt (CBM) of MBT and a minimum of 14% MBT (CBM gives MBT on h.p.l.c. analysis). Acetone (5 $cm^3$) was added to the filtrate: there was no further precipitation. The solvent was evaporated and boiling dichloromethane (5 $cm^3$) added to the residue. On cooling, a solid was filtered off. By h.p.l.c. analysis, this was by weight 3.2% MBTS (26 mol% in total recovered), a maximum of 73% CBM (a maximum of 32 mol% altogether), and a minimum of 24% MBT (a minimum of 21 mol% altogether). The filtrate was eluted with dichloromethane on a silica gel column. Three main fractions (19, 91 and 70 mg) were collected. The second was purified by elution with dichloromethane through a second silica gel column and then recrystallised from petroleum ether (b.p. 40°C - 60°C) giving 2'-benzothiazolylthiopropan-2-one (**1**) (23.3 mg, 5.2%), m.p. 68°C - 69°C (*Reference 5*, 70°C - 71°C); $\nu_{max}$ (KBr) 2960, 1725 (CO), 1470, 1435, 1365, 1320, 1300, 1280, 1240, 1005 (C-S), and 760 $cm^{-1}$ (*Reference 5*, 1720 $cm^{-1}$); $\delta_H$ (90 MHz; $CDCl_3$) 2.35 (3H, s, $CH_3$), 4.20 (2H, s, $CH_2$), and 7.2-7.9 (4H, m, ArH). The third fraction was recrystallised from ethyl acetate giving 1, 1-*bis*-(2'-*benzothiazolylthio*)-2-*cyclo-hexylaminoprop*-1-*ene* (**2**) (16.9 mg, 3.6%), m.p. 206°C-207°C (with some decomposition). It can be further recrystallised from acetone raising the m.p. to 209.8°C-210.2°C (Found: C, 59.0; H, 5.0; N, 9.2. $C_{23}H_{23}N_3S_4$ requires C, 58.8; H, 4.9; N, 8.9%); $\nu_{max}$ (KBr) 3240 (NH), 2930, 2850, 1560, 1460, 1425, 1005 (C-S), 760, 750 and 725 $cm^{-1}$; $\lambda_{max}$ (EtOH) 226 nm; $\delta_H$ (200 MHz; $CDCl_3$) 1.0-2.0 [10H, m, $(CH_2)_5$], 2.46 (3H, s, $CH_3$), 3.39 (1H, m, NCH), 6.34 (1H, d, *J* 9 Hz, NH, exchanges with $D_2O$), 7.29 and 7.41 (4H, 2xt, *J* 7 Hz, 5'-H and 6'-H), 7.76 (2H, d, *J* 8 Hz, 4'-H or 7'-H) and 7.85 (2H, dd, *J* 8 and 3 Hz, 4'-H or 7'-H); $\delta_c$ (50.3 MHz; $CDCl_3$) 24.7 (cyclohexyl C-3 and C-5), 25.1 (cyclohexyl C-4). 34.3 (cyclohexyl C-2 and C-6), 53.7 (NCH), 108.1 (C=*C*Me), 120.9 and 121.0 (C-4'), 121.7 (C-7'), 123.7 and 124.0 (C-6'), 126.0 (C-5'), 135.4 and 135.5 (C-7a'), 155.4 and 155.7 (C-3a'), 166.3 (*C*=CMe), and 172.3 and 176.2 (C-2').

**Reaction of MBTS with Acetone**

MBTS (664 mg, 2 mmol) and acetone (5.08 g) were stirred at room temperature for 67 h. The solid (634 mg) was filtered off and the solvent evaporated from the filtrate. The filtered solid and the residue (13 mg) from the filtrate were both MBTS by t.l.c.

**Reaction of CBS with Acetone**

A solution of CBS (1.32 g, 5 mmol) in acetone (60 $cm^3$) was stirred at room temperature for 24 h with exclusion of light. (The product **2** is sensitive to light: when exposed, it turns yellow.) The precipitate (308 mg) was filtered off and recrystallised from acetone. This was the enamine (**2**) and was identical (by i.r. spectroscopy) with samples obtained previously. The filtrate of the reaction mixture was reduced to *ca.* 10 $cm^3$ and cooled in the refrigerator (0°C) to precipitate more of **2** (46 mg). Repeating this process yielded a third crop of **2** (23 mg). The solvent was evaporated from the final filtrate. The residue was dissolved in diethyl ether (30 $cm^3$) and extracted with aqueous sodium dihydrogen phosphate, dihydrate (0.1*M*, 3 × 30 $cm^3$), and

then with aqueous sodium hydroxide (2.5 *M*, 3 × 15 $cm^3$). The pH of the combined sodium dihydrogen phosphate extracts was adjusted to 12 with aqueous sodium hydroxide (2.5*M*) and the ketone (**1**) (30 mg) (identified by i.r. spectroscopy) filtered off. Benzoyl chloride (2 $cm^3$) was added to the filtrate and the mixture shaken for 10 min. This gave *N*-cyclohexylbenzamide (313 mg, 31%), which was filtered off and recrystallised from aqueous ethanol giving 221 mg (22%), m.p. 146.1°C–148.4°C (*Reference 4*, m.p. 147°C); the i.r. spectrum was identical to that of an authentic sample prepared from cyclohexylamine, benzoyl chloride and aqueous NaOH. The combined sodium hydroxide extracts were acidified with hydrochloric acid (2*M*). MBT (12 mg, 1.4%) was filtered off; the i.r. spectrum was identical to a reference spectrum. The solvent was evaporated from the ethereal solution and the residue eluted with dichloromethane on a silica gel column. The first fraction was the ketone (**1**) (403 mg, total yield 433 mg, 39%), which was recrystallised from petroleum ether (b.p. 40°C–60°C) and was identical (by i.r. spectroscopy) to samples obtained previously. The next fraction was triturated with petroleum ether (b.p. 40°C–60°C yielding more **2** (8 mg, total yield 385 mg, 33%).

This reaction was carried out several times. On the other occasions, similar amounts of **2** and higher yields (up to 62%) of **1** were obtained, but yields of MBT and cyclohexylamine (as its benzamide) were not determined.

**Reaction of 2′-benzothiazolylthiopropan-2-one (1) with CBS**

*In the presence of cyclohexylamine.* CBS (2.64 g, 10.0 mmol) dissolved in diethyl ether (225 $cm^3$), **1** (2.24 g, 10.0 mmol) in diethyl ether (70 $cm^3$), and cyclohexylamine (0.997 g, 10.05 mmol) were combined together and stirred at room temperature in the dark. After six days, the precipitate was filtered off. By $^1$H NMR spectroscopy, this was a mixture of the enamine (**2**) (2.87 g) and 1,1-*bis*-(2′-*benzothiazolylthio*)-*propan*-2-*one* (**4**) (1.07 g, 28%). These were separated by eluting on a silica gel column with dichloromethane. **4** (0.53 g, 14%) eluted first and was recrystallised from petroleum ether (40°C–60°C), m.p. 87.0°C–87.7°C (Found: C, 52.5; H, 3.1; H, 7.4. $C_{17}H_{12}N_2OS_4$ requires C, 52.6; H, 3.1; N, 7.2%); $\upsilon_{max}$ (KBr) 1735(CO), 1460, 1430, 995 and 755 $cm^{-1}$; $\delta_H$ (90 MHz; $CDCl_3$) 2.59 (3H, s, $CH_3$), 6.68 (1H, s. CH), 7.1–7.5 (4H, m, 5′-H and 6′-H) and 7.6–7.9 (4H, m, 4′-H and 7′-H). **2** (2.72 g, 58%) eluted later and was recrystallised from acetone, m.p. 201.8°C–202.5°C; i.r. and $^1$H NMR spectra were identical with those of earlier samples.

The filtrate from the reaction mixture was reduced to 30 $cm^3$ and extracted successively with aqueous sodium dihydrogen phosphate, dihydrate (1*M*, 3 × 30 $cm^3$), aqueous sodium hydroxide (1*M*, 3 × 15 $cm^3$) and water (3 × 10 $cm^3$). The phosphate extracts were combined and their pH adjusted to 11.5 with aqueous sodium hydroxide (1*M*). Benzoyl chloride (4 $cm^3$) was added to this in 1 $cm^3$ portions and the mixture shaken for 10 min. *N*-cyclohexylbenzamide (2.26 g) was filtered off (i.r. spectrum was identical with that of an authentic sample). The combined sodium hydroxide extracts were acidified with hydrochloric acid (2*M*). MBT (0.7 mg, 0.04%) was filtered off. During extraction, a precipitate appeared in the ethereal layer. This was filtered off and shown by $^1$H NMR spectroscopy and t.l.c. to be **2** (109 mg). More **2** (17 mg) precipitated from the new filtrate on standing. After filtering this off, the ether was evaporated and the residue eluted on a silica gel column with dichloromethane. The first main fraction was unreacted CBS (59 mg, 2.2%). The last fraction collected was **2** (36 mg, total yield 65%, or 66% based on CBS consumed).

The intermediate fractions were rechromatographed on silica gel eluting with dichoromethane/petroleum ether (b.p. 40°C–60°C) (50:50). The first main fraction was unreacted **1** (31 mg, 1.4%). Next was 1,3-bis (2′-benzothiazolylthio) propan-2-one (**3**) (165 mg, 4.2%, or 4.3% based on CBS consumed), which was recrystallised from cyclohexane, m.p. 127.9°C–128.0°C

(*Reference 6*, m.p. 127°C) (Found: C, 52.7; H, 3.3; N, 7.1. Calculated for $C_{17}H_{12}N_2OS_4$: C, 52.6; H, 3.1; N, 7.2%); $\upsilon_{max}$(KBr) 2940, 2895, 1730(CO), 1460, 1425, 1000 and 755 $cm^{-1}$; $\delta_H$(400 MHz; $CDCl_3$) 4.50 (4H, s, $CH_2$), 7.30 (2H, ddd, *J* 1.2, 7 and 8 Hz, 5′-H or 6′-H) 7.40 (2H, ddd, *J* 1.3, 7 and 8 Hz, 5′-H or 6′-H), and 7.75 and 7.82 (4H, 2xd, *J* 8 Hz, 4′-H and 7′-H).

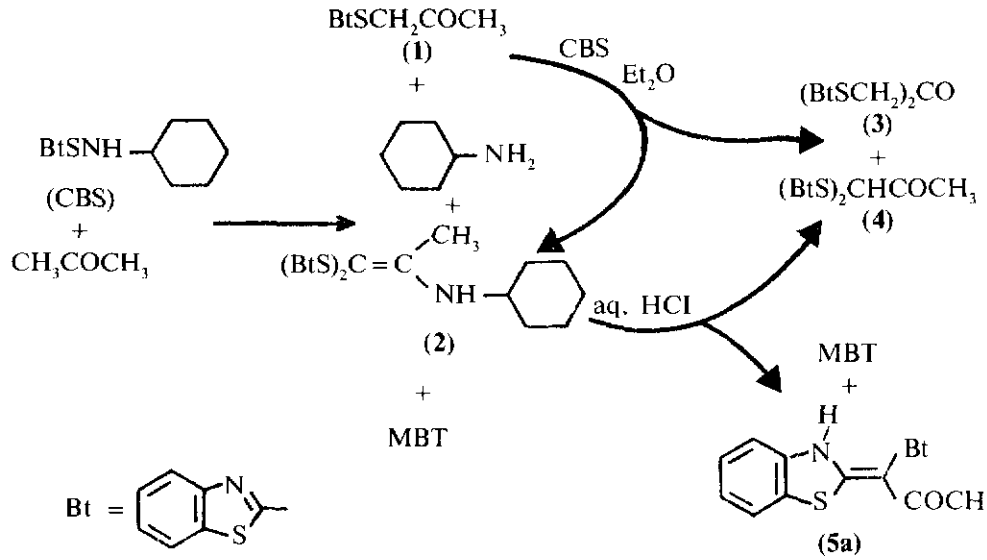
*In the absence of cyclohexylamine.* CBS (132.5 mg, 0.50 mmol) in diethyl ether (30 $cm^3$) and **1** (111.6 mg, 0.50 mmol) were stirred together at room temperature in the dark for fourteen days. The precipitate was filtered off. By $^1H$ NMR spectroscopy, this was a mixture of **2** (113.3 mg) and **4** (24.1 mg, 12%), which can be separated by eluting with $CH_2Cl_2$ on silica gel as described above. The solvent was evaporated from the filtrate from the reaction mixture and the residue subjected to preparative t.l.c. on silica gel eluting seven times with $CH_2Cl_2$. *Fraction 4* was **3** (14.5 mg, 4.3%). *Fraction 6* was recrystallised from chloroform yielding MBT (0.7 mg, 0.8%), m.p. 181.5°C–181.9°C (*Reference 4*, m.p. 177°C–179°C). *Fraction 8* was **2** (14.1 mg, total yield 127.1 mg, 54%).

**Hydrolysis of 1, 1-bis-(2′benzothiazolylthio)-2-cyclohexyl-aminoprop-1-ene (2)**

A solution of the enamine (**2**) (940 mg, 2 mmol) in dichloromethane (150 $cm^3$) was stirred with hydrochloric acid (2*M*, 50 $cm^3$) initially at room temperature for eleven days and then under reflux for 117 h. The organic layer was washed with aqueous saturated sodium bicarbonate (75 $cm^3$) and water (2 × 75 $cm^3$), and dried ($MgSO_4$). The solvent was evaporated and the residue eluted on a silica gel column with dichloromethane. The sixth fraction was the ketone (**4**) (380 mg, 49%), which was recrystallised from petroleum ether (b.p. 40°C–60°C), m.p. 84.6°C–85.0°C, the i.r. spectrum was identical to that of the sample obtained above. The seventh fraction was MBT (60 mg, 9%) and was recrystallised from chloroform, m.p. 179.2°C–181.3°C (*Reference 4*, 177°C–179°C), i.r. and NMR spectra were identical with reference spectra. The eighth fraction was (E)-1-2′-*benzothiazolyl*-1-2′ (3′ H)-*benzothiazolylidene*-2-*propanone* (**5a**) (40 mg, 6%), which was recrystallised twice from cyclohexane and then twice from ethanol, m.p. 187.9°C–188.4°C (*Reference 7*, m.p. 185°C) (Found: C, 62.8; H, 3.9; N, 8.5. $C_{17}H_{12}N_2OS_2$ requires C, 62.9; H, 3.7; N, 8.6%); $\upsilon_{max}$ (KBr) 3430 (NH), 1605, 1500, 1455, 1435, 1375 and 740 $cm^{-1}$; $\lambda_{max}$(EtOH) 365 nm; $\delta_H$(300 MHz; $CDCl_3$) 2.81 (3H, s, $CH_3$), 7.33 and 7.49 (4H, 2xt, *J* 7 Hz, 5′-H and 6′-H), 7.77 and 7.82 (4H, 2xd, *J* 8 Hz, 4′-H and 7′-H), and 16.05 (1H, s, OH). In $CDCl_3$, this contained 14% of a mixture of the tautomers (**5b** and **5c**); $\delta_H$(300 MHz) 2.63 (3H, s, $CH_3$), 7.4 (4H, 2xt, 5′-H and 6′-H), 7.61, 7.74, 7.88 and 8.05 (4H, 4xd, *J* 8Hz, 4′-H and 7′-H), and 15.87 (1H, s, NH or OH). Small quantities of several other products were also obtained from the column, but they were insufficient for full characterisation.

## RESULTS AND DISCUSSION

No reaction was detected between MBTS and acetone after 67 h at room temperature, although MBTS is fairly insoluble in acetone at room temperature and only about 2% was in solution. On the other hand, CBS which is more soluble, reacted readily with acetone and all had reacted after about 24 h at room temperature. Two main products were obtained. One (**2**) precipitated out of the reaction mixture in a yield of 33%. Its $^1H$ and $^{13}C$ NMR spectra revealed the presence of two benzothiazole groups, a methyl and a cyclohexylamino group. In the $^{13}C$ spectrum, most of the benzothiazole carbons appear as doublets implying that the two groups have slightly different environments; two additional downfield resonances are also present. The i.r. spectrum confirmed the presence of the amino and benzothiazol-2-ylthio groups, and a u.v. absorption at 226 nm is also consistent with two substituted benzothiazolyl groups. The proposed structure (**2**) was eventually established by elemental analysis. The other main product was identified as the ketone (**1**) and was isolated by column chromatography in yields of up to 62%. Also produced were cyclohexylamine and a trace (1.4%) of MBT (isolated as such but presumably present in the




product mixture as its cyclohexylammonium salt). The cyclohexylamine was isolated as its benzoyl derivative (31%).

It would seem likely that the ketone (**1**) is an intermediate in the formation of the enamine (**2**) from CBS. To confirm this, the reaction of **1** with CBS in the absence of acetone was investigated. Instead of acetone, an inert solvent, diethyl ether, was used. The reaction took two weeks to go to completion, but as predicted **2** was obtained in 54% yield together with a trace (0.8%) of MBT and two other minor products. These were characterised as 1,3-bis-(2′-benzothiazolylthio) propan-2-one (**3**)[6] and 1,1-bis-(2′-benzothiazolylthio) propan-2-one. As mentioned above, cyclohexylamine is a by-product of the reaction of CBS and acetone. It was found to catalyse the reaction of **1** with CBS, although complete reaction still took six days. **2** (66%), **3** (4.3%), **4** (28%) and MBT (0.04%) were all isolated.

**3** and **4** were not originally detected in the reaction between CBS and acetone. On re-investigation, a trace (0.3%) of **3** was found. **4** was not found, but as **2** and **4** have apparently identical retention on silica gel, a trace of **4** in the reaction would be difficult to detect. At least part of the explanation for the significant yield of **4** from the reaction between CBS and **1** in diethyl ether may be solubility. Both **2** and **4** are virtually insoluble in diethyl ether and would precipitate out when formed. In contrast, in acetone, **2** is also insoluble while **4** is soluble, thus an equilibrium between **2** and **4** would favour **2** in acetone.

To provide further confirmation for the proposed structure (**2**), the enamine was hydrolysed with aqueous hydrochloric acid. The hydrolysis was slow, but the expected product (**4**) was obtained in 49% yield. A large number of minor by-products were also obtained. Two were identified: one was MBT (9%) and the other was characterised as (*E*)-1-2′-benzothiazolyl-1-2′ (3′*H*)-benzothiazolylidene-2-propanone (**5a**). The unexpected absence of benzothiazolylthio groups in the latter was indicated by the lack of a characteristic C-S i.r. absorption at about 1000 cm $^{-1}$, and confirmed by the elemental analysis. This compound (**5a**) has been obtained previously[7], but was assigned the (*Z*)-tautomeric structure (**5c**). The present assignment [predominantly the (*E*)-tautomer (**5a**)] is based on NMR spectroscopy in various solvents (*Table 1*).

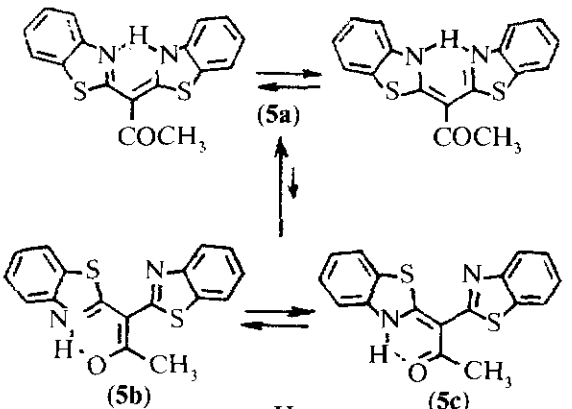
In $CDCl_3$, two sets of signals in the ratio 86:14 are visible. In the major group, the corresponding protons of the two benzothiazole

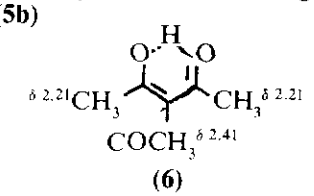
TABLE 1. $^1$H NMR SPECTRAL SIGNALS OF 5 δ (p.p.m.)

| Solvent | $CH_3$ | | 5-H, 6-H | | 4-H, 7-H | | OH/NH | |
|---|---|---|---|---|---|---|---|---|
| | **5a** | **5b/5c** | **5a** | **5b/5c** | **5a** | **5b/5c** | **5a** | **5b/5c** |
| $(CD_3)_2SO$ | 2.60 | - | 7.38 | 7.54 | 8.04 | - | 14.87 | - |
| $(CD_3)_2CO$ | 2.74 | - | 7.40 | 7.55 | 8.01 | - | 15.89 | - |
| $CDCl_3$ | 2.81 | 2.63 | 7.33 | 7.49 | 7.77, 7.82 | 7.61, 7.74, 7.88, 8.05 | 16.05 | 15.87 |
| $CD_2Cl_2$ | 2.79 | 2.64 | 7.35 | 7.51 | 7.83, 7.86 | 7.67, 7.81, 7.92, 8.03 | 16.02 | a |
| $C_6D_6$ | 2.64 | 2.45 | 6.94 | 7.11 | 7.31, 7.36 | S, S, 7.51, 8.17 | a | a |

S Submerged under other signals
[a]Not observed

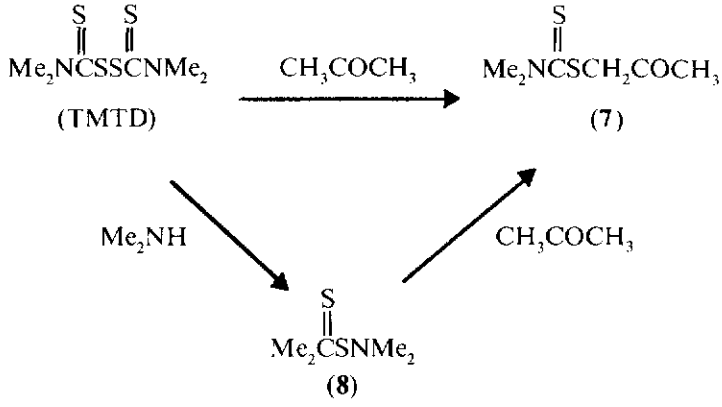
groups are equivalent, while in the minor group, the protons at the 4- and 7- positions are not equivalent. In more polar solvents ($CD_3COCD_3$ and $CD_3SOCD_3$), the minor signals disappear, whereas in the less polar $CD_2Cl_2$ and $C_6D_6$, their contributions increase to 15% and 23%, respectively. Proton transfer between the nitrogens in 5a would be expected to be fast on the NMR time scale leading to equivalence of the benzothiazole groups. Proton transfer between oxygen and nitrogen in the equilibrium of **5b** and **5c** should also be fast but here the benzothiazole groups will retain their non-equivalence. Consequently, the major NMR signals are assigned to the (*E*)-tautomer (**5a**), and the minor signals appearing in the less polar solvents to an equilibrium of **5b** and **5c**. These assignments are supported by the chemical shifts of the methyl groups. Based on the spectrum of triacetylmethane (**6**), the protons of the acetyl group in **5a** would be expected to be shifted downfield from those of the hydrogen-bonded acetyl/enol groups in **5b/5c**. The effect of solvent polarity on the tautomeric equilibria suggests that there is a significant content of **5b** in the **5b/5c** equilibrium, as **5b** would probably have the least contribution from zwitterionic canonical forms of the three tautomers.




(6)

As mentioned in the introduction, Jefferson *et al.*[3] have observed previously that TMTD undergoes a reaction similar to the formation of **1** from CBS. The ketone (**7**) is produced from TMTD after four days at room temperature, which is a little slower than the formation of **1** from CBS. However, they found that the sulphenamide (**8**) reacts very rapidly with acetone, the reaction taking only 10 min at room temperature. This suggests that TMTD itself reacts with acetone *via* the sulphenamide (**8**), as any dimethylamine, present as an impurity or produced from TMTD, would readily lead to the formation of **8** which in turn would rapidly react with acetone regenerating the amine.




## CONCLUSIONS

CBS has been found to react with acetone at room temperature to give the ketone (**1**), the enamine (**2**), cyclohexylamine and a trace of MBT. **2** was shown to be produced *via* **1**. Based on this and previous work[3], the order of reactivity of different types of accelerator towards acetone appears to be MBTS < thiuram disulphides < benzothiazolesulphenamides < thiocarbamoylsulphenamides. This reactivity should be borne in mind when employing acetone extraction in the analysis of curatives in rubber compounds or vulcanisates.

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