THE REACTION OF TETRAMETHYLTHIURAMDISULPHIDE WITH ACETONE

I. REACTION PRODUCTS[1]

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ABSTRACT

Tetramethylthiuramdisulphide reacts with acetone to form various dithiocarbamate derivatives of acetone, dimethylamine, and carbon disulphide. The reaction has an induction period which is markedly influenced by various additives. The reaction products, their properties and synthesis, are described.

Tetramethylthiuramdisulphide, "TMTD" or "*bis*-(dimethylthiocarbamoyl)-disulphide", is well known as a vulcanization accelerator and as a potent fungicide. In handling hot acetone solutions of the material we have observed evidence of rapid decomposition; even at room temperature, discoloration occurs in a few hours. A survey of the literature indicates that other workers have noted this instability (4, 5, 7, 8) but no one appears to have reported on the composition of the reaction products. An investigation of the process was considered worth while as it might help to elucidate the chemical behavior of TMTD as an accelerator and a fungicide.

DISCUSSION

We have found that TMTD (I) reacts with refluxing acetone to form 1-(dimethylthiocarbamoylthio)-2-propanone (II), dimethylammonium dimethyldithiocarbamate (IV), dimethylamine, carbon disulphide, 1,3-*bis*-(dimethylthiocarbamoylthio)-2-dimethylamino-1-propene (V), and 1,3-*bis*-(dimethylthiocarbamoylthio)-2-propanone (VI). There was no evidence of a 1,1-isomer of VI, and we were unable to isolate the expected monosubstituted propene, VII. The enamine (V) readily hydrolyzes to the propanone derivative VI.

Several grades of acetone were tried including material purified through the bisulphite compound, "Spectro Grade", "Certified Reagent Grade", and commercial amine-free acetone (Carbide and Carbon Chemical Corporation, C.P. grade). The latter material was used for the experiments reported here, as all grades gave the same products. In paper II of this series (3) (Table I), the effect of water upon the reaction is shown to be relatively small, so no attempt was made to dry the acetone.

On the basis of earlier studies of the TMTD vulcanization of rubber (1, 2) we also expected to find sulphur, tetramethylthiurammonosulphide, dimethyl-

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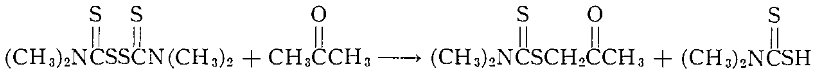
thiocarbamoyldimethylsulphenamide, and tetramethylthiourea; none of these materials was found, nor was acetonylacetone.

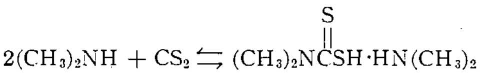
We were unable to form the disubstituted compound VI by treating the monosubstituted acetone (II) with excess TMTD in dry benzene; similarly, the reverse attempt to form II by refluxing VI with acetone failed. Attempts to synthesize the propene derivative (V) by treatment of VI with dimethylamine in the presence of dehydrating agents were unsuccessful.



$$\mathrm{(CH_3)_2N\overset{S}{\overset{\|}{C}}S S\overset{S}{\overset{\|}{C}}N(CH_3)_2 + CH_3\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow (CH_3)_2N\overset{S}{\overset{\|}{C}}SCH_2\overset{O}{\overset{\|}{C}}CH_3 + (CH_3)_2N\overset{S}{\overset{\|}{C}}SH}$$

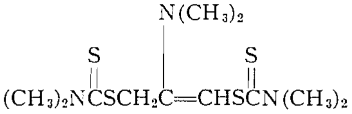
I II III

$$\mathrm{III \longrightarrow (CH_3)_2NH + CS_2}$$



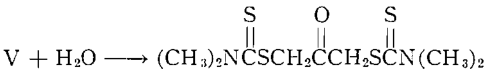
$$\mathrm{2(CH_3)_2NH + CS_2 \leftrightarrows (CH_3)_2N\overset{S}{\overset{\|}{C}}SH\cdot HN(CH_3)_2}$$

IV



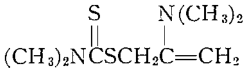
$$\mathrm{(CH_3)_2N\overset{S}{\overset{\|}{C}}SCH_2\overset{N(CH_3)_2}{\overset{|}{C}}{=}CHS\overset{S}{\overset{\|}{C}}N(CH_3)_2}$$

V



$$\mathrm{V + H_2O \longrightarrow (CH_3)_2N\overset{S}{\overset{\|}{C}}SCH_2\overset{O}{\overset{\|}{C}}CH_2S\overset{S}{\overset{\|}{C}}N(CH_3)_2}$$

VI



$$\mathrm{(CH_3)_2N\overset{S}{\overset{\|}{C}}SCH_2\overset{N(CH_3)_2}{\overset{|}{C}}{=}CH_2}$$

VII

The structures of the mono- and di-substituted acetones (II and VI) were confirmed by synthesis from the appropriate chloro- and bromo-acetones, using the method of Nachmias (6) who reported II but not VI.

The TMTD–acetone reaction exhibits an induction period the length of which can be completely controlled by the use of suitable additives. The most potent activator of the reaction is dimethylamine, or its salt, dimethylammonium dimethyldithiocarbamate (IV). Since most samples of TMTD contain varying amounts of IV as an impurity, different induction periods will be noted with different samples, as the influence of IV is proportional to its concentration. The addition of acetic anhydride, on the other hand, will inhibit the reaction indefinitely. A more detailed study of the influence of additives may be found in paper II of this series.[4]

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[4] *See the next paper in this Journal.*

EXPERIMENTAL

1-(Dimethylthiocarbamoylthio)-2-propanone (II)

A mixture of 24.0 gm. (0.1 mole) of TMTD and 60 ml. of benzene was refluxed for 2.5 hr. during the addition of 6.4 gm. (0.11 mole) of acetone. Refluxing was continued for one hour. The mixture was cooled to 10° and filtered to give 6.6 gm. of dimethylammonium dimethyldithiocarbamate (IV) which melted at 131–135° with decomposition. The filtrate, containing CS_2, was distilled until nearly all the benzene was removed. The addition of ether caused the slow crystallization of Crop 1, 0.5 gm., m.p. 150–152°. The filtrate on evaporation gave 4.5 gm. of solid (Crop 2), which melted at 47–50° and at 58° after crystallization first from water and then from alcohol–water mixture. Anal. Calc. for $C_6H_{11}NOS_2$: C, 40.63; H, 6.26; N, 7.90; S, 36.18%. Found: C, 40.50; H, 6.26; N, 7.89; S, 36.24%.

The compound thus analyzes for 1-(dimethylthiocarbamoylthio)-2-propanone or "acetonyldimethyldithiocarbamate" (II), a compound reported by Nachmias (6) as the reaction product of sodium dimethyldithiocarbamate and monochloracetone. Using his method, we secured II in 90% yield, melting at 58° alone or mixed with the II from Crop 2 above. We have not observed the melting point of 73° reported by him. Dr. A. Quevauviller has forwarded to us a sample of the Nachmias compound. We found it to melt at 58° alone or mixed with our II. The material fails to give the iodoform test. It is soluble in hot water and most organic solvents.

1,3-bis-(Dimethylthiocarbamoylthio)-2-propanone (VI)

The filtrate from Crop 2 (above), on standing, deposited a further 0.6 gm. of crystals melting at 150–152° alone or mixed with Crop 1. Recrystallization from alcohol gave colorless needles, m.p. 158°. Anal. Calc. for $C_9H_{16}N_2OS_4$: C, 36.45; H, 5.43; N, 9.45; S, 43.25%. Found: C, 36.55; H, 5.42; N, 9.34; S, 43.19%.

This compound is quite soluble in benzene, slightly soluble in alcohol, and nearly insoluble in hexane, water, and ether. Samples prepared by the method of Nachmias (6) from 1,3-dihalo-2-propanones melted at 158° alone or mixed with VI from Crop 1 above.

Significantly higher yields of both II and VI were later obtained by eliminating the benzene and simply refluxing an acetone solution of TMTD. After an initial induction period, the same products were formed. The reaction was greatly accelerated (shown by earlier color development, amine and CS_2 formation) by the addition of a crystal of dimethylammonium dimethyldithiocarbamate. The acetone was then evaporated, the products extracted from the residue with appropriate solvents and recrystallized as described above.

1,3-bis-(Dimethylthiocarbamoylthio)-2-dimethylamino-1-propene (V)

In some experiments, difficulty was encountered in separating II from VI and resort was made to alcohol for crystallization. Needles mixed with well-defined granular crystals appeared. The granules (V) were separated (physically) from the needles (VI) and, after two recrystallizations from alcohol, they melted at 102–103°. Anal. Calc. for $C_{11}H_{21}N_3S_4$: C, 40.83; H, 6.55; N, 12.98%. Found: C, 40.68; H, 6.61; N, 12.55%.

Conversion of V to VI

Compound V, 0.0605 gm., 2 ml. of alcohol, and one drop of aqueous acetic acid were refluxed for two minutes and the solvent evaporated. Recrystallization of the residue gave 0.054 gm. (98%) of colorless needles, m.p. 156–158° alone or mixed with VI.

Acetone and VI

A solution of 262 mgm. (0.883 mmole) of VI in 20 ml. of acetone was refluxed for 24 hr. It was cooled and the acetone evaporated under a stream of nitrogen. The residue was recrystallized from ethanol resulting in a 95% recovery of VI, m.p. 156–157°.

A similar experiment in which 15.4 mgm. (0.092 mmole) of dimethylammonium dimethyldithiocarbamate was included produced the same result. Obviously VI is not readily converted to II in excess acetone.

Tetramethylthiuramdisulphide (TMTD) and II

A solution of 240 mgm. (1.0 mmole) of TMTD and 177.3 mgm. (1.0 mmole) of II in 15 ml. of dry benzene was refluxed for 20 hr. On evaporation of the solvent, II was first recovered from the residue by leaching with warm water, producing needles, m.p. 56–58°. The final residue was then recrystallized from ethanol and 220 mgm. (92%) of TMTD, m.p. 156–157° alone or mixed with an authentic sample, was recovered.

Another run which included 3.8 mgm. (0.02 mmole) of dimethylammonium dimethyldithiocarbamate gave similar results. In neither case was there any evidence of the production of compound VI from II.

Attempted Synthesis of V

Compound VI, 381 mgm. (1.28 mmole), was dissolved in 500 ml. of absolute ethanol and treated with a large excess (25 ml.) of anhydrous dimethylamine. Anhydrous $MgSO_4$, 15 gm., was added and the suspension was placed on the shaker for 30 hr. at room temperature. After it was allowed to stand an additional $1\frac{1}{2}$ days, the drying agent was filtered off and the solvent and excess dimethylamine evaporated under dry nitrogen. The residue consisted of 360 mgm. of starting material, m.p. 156°. Refluxing with K_2CO_3 gave similar results.

Spectra

Absorption spectra of some of the products are given below.

The significant infrared absorption peaks[5] of chloroform solutions of II, IV,

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[5] *The infrared data were obtained using a Perkin-Elmer No. 21 double beam recording spectrophotometer. The authors are indebted to Mr. R. W. White, Science Service Laboratory, for recording these data.*

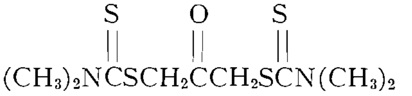
and VI are as follows, where S, M, and W indicate a strong, medium, and weak absorption:

$$II = (CH_3)_2N\overset{S}{\overset{\|}{C}}SCH_2\overset{O}{\overset{\|}{C}}CH_3$$

2920M, 1715S, 1495S, 1407W, 1380S, 1357S, 1277W,
1225*, 1150S, 1050W, 980S, 867W cm.$^{-1}$

$$IV = (CH_3)_2N\overset{S}{\overset{\|}{C}}SH{\cdot}HN(CH_3)_2$$

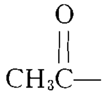
2920S, 2670S, 2390M, 1485M, 1465S, 1410W, 1365S, 1245S,
1215*, 1120S, 1040W, 1025M, 967S, 890M, 660W cm.$^{-1}$



$$VI = (CH_3)_2N\overset{S}{\overset{\|}{C}}SCH_2\overset{O}{\overset{\|}{C}}CH_2S\overset{S}{\overset{\|}{C}}N(CH_3)_2$$

2920M, 1717M, 1495S, 1407W, 1380S, 1290W,
1225*, 1147S, 1040M, 982S, 895M cm.$^{-1}$

A value marked with an asterisk is approximate, the exact peak being partially obscured by one due to chloroform.



The peak at 1357 cm.$^{-1}$ is due to the $CH_3\overset{O}{\overset{\|}{C}}$—group and its presence in II and absence in VI confirms the symmetrical structure of VI.

In the near infrared[6] region of the spectrum freshly prepared acetone solutions of I, II, IV, VI, dimethylamine, and sodium dimethyldithiocarbamate exhibit no absorption. After two weeks at room temperature absorption peaks occur at 2620–2680, 2195, 2060, 1925, 1775, 1725, and 1435 millimicrons in all of the solutions. A similar absorption spectrum is obtained from acetone which has been refluxed with barium hydroxide, a procedure known to favor the production of diacetone alcohol.

In the ultraviolet region,[6] freshly prepared ethanol solutions of II, IV, and VI exhibit strong absorption with maxima at the following wavelengths:

IV: 289 and 254 millimicrons, both of which disappear when the solutions are left overnight at room temperature.

II and VI: 276, 246, and 216 millimicrons. These solutions appear to be stable.

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[6] *Ultraviolet and near-infrared data were obtained using a Beckman DK-1 recording spectrophotometer.*