LXXVI.—*Some Thio- and Dithio-carbamide Derivatives of Ethyleneaniline and the Ethylenetoluidines.*

By OLIVER CHARLES MINTY DAVIS.

ETHYLENEANILINE and the ethylenetoluidines interact with the thio-carbimides to give crystalline compounds. In most cases when the change is effected by heating the two reagents on a water-bath at 100°, a quantitative yield is obtained. With few exceptions the product could be obtained in a state of comparative purity by washing with cold alcohol, and this method was used in each case before recrystallising for analysis.

During the investigation, several instances of steric hindrance were observed, the position of the substituent methyl group in the ethylenetoluidines and the tolylthiocarbimides having an important bearing both on the time of reaction and also on the nature of the product. One molecule of ethyleneaniline unites with two molecules of allyl-, phenyl-, *o*-tolyl-, or *p*-tolyl-thiocarbimide to form symmetrical dithio-

carbamide derivatives, but with *m*-tolylthiocarbimide only one molecule of each unites to form an asymmetrical, substituted thiocarbamide. Ethylene-*o*-toluidine interacts with difficulty to give asymmetrical derivatives in the case of phenyl-, *m*-tolyl-, and *p*-tolyl-thiocarbimides, but with allyl- and *o*-tolyl-thiocarbimides the yield of product was very small, and the substance could not be purified for analysis.

Ethylene-*m*-toluidine gives symmetrical derivatives with phenyl- and *p*-tolyl-thiocarbimides, but with the allyl, *o*-tolyl, and *m*-tolyl compounds asymmetrical derivatives result.

Ethylene-*p*-toluidine gives an asymmetrical derivative with *m*-tolyl-thiocarbimide, but with its analogues symmetrical derivatives are formed.

With the ethylenetoluidines, the ortho- and meta-positions therefore seem to modify the reactions, but in the thiocarbimides the meta-position only has this effect. When heated in alcoholic solution with mercuric oxide to about 140°, the thiocarbamide derivatives yield the corresponding oxygen compounds. The product obtained from the interaction of ethyleneaniline and phenylthiocarbimide appears to be identical with a compound synthesised from ethyleneaniline and phenylcarbimide. This fact strengthens the supposition that the compounds described are thio- and dithio-carbamide derivatives, their constitution being represented by the general formulæ

The table on p. 715 indicates the nature of the compound formed in each case.

EXPERIMENTAL.

Ethyleneaniline and Allylthiocarbimide.—These reagents when heated together for about half an hour at 100° readily interact, yielding a crystalline product. The reaction was carried out under varying conditions, using either excess of ethyleneaniline or excess of the thiocarbimide, but in all cases the chief product is a crystalline compound formed by the union of 1 molecule of ethyleneaniline and 2 of the thiocarbimide. This substance is best recrystallised from absolute alcohol, and is obtained in well-defined needles, very soluble in acetone and benzene, and melts without decomposition at 165°.

0.2764 gave 0.6500 CO₂ and 0.1704 H₂O. C = 64.15; H = 6.84.

0.1482 „ 0.1631 BaSO₄. S = 15.11.

0.1630 „ 19.6 c.c. moist nitrogen at 23° and 766 mm. N = 13.65.

C₂₂H₂₆N₄S₂ requires C = 64.39; H = 6.34; N = 13.65; S = 15.60 per cent.

A molecular weight determination, using the ebullioscopic method

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Ethylene compound.	Thiocarbimide.	Thiocarbamide.	Melting point.	
			Sym- metrical.	Asym- metrical.
Ethylene aniline.....	Allyl	$C_2H_4(NPh \cdot CS \cdot NH \cdot C_3H_5)_2$	165°	—
„ „	Phenyl	$C_2H_4(NPh \cdot CS \cdot NHPh)_2$	184	—
„ „	<i>o</i> -Tolyl.....	$C_2H_4[NPh \cdot CS \cdot NH \cdot C_7H_7(o)]_2$	179	—
„ „	<i>m</i> -Tolyl	$C_2H_4 \begin{smallmatrix} \diagup NPh \cdot CS \cdot NH \cdot C_7H_7 \\ \diagdown NHPh \end{smallmatrix}$	—	185°
„ „	<i>p</i> -Tolyl	$C_2H_4(NPh \cdot CS \cdot NH \cdot C_7H_7)_2$	190	—
Ethylene- <i>o</i> -toluidine.	Phenyl	$C_2H_4 \begin{smallmatrix} \diagup N(C_7H_7) \cdot CS \cdot NHPh \\ \diagdown NH \cdot C_7H_7 \end{smallmatrix}$	—	150
„ „	<i>m</i> -Tolyl	$C_2H_4 \begin{smallmatrix} \diagup N(C_7H_7) \cdot CS \cdot NH \cdot C_7H_7 \\ \diagdown NH \cdot C_7H_7 \end{smallmatrix}$	—	157
„ „	<i>p</i> -Tolyl	$C_2H_4 \begin{smallmatrix} \diagup N(C_7H_7) \cdot CS \cdot NH \cdot C_7H_7 \\ \diagdown NH \cdot C_7H_7 \end{smallmatrix}$	—	118
Ethylene- <i>m</i> -toluidine	Allyl	$C_2H_4 \begin{smallmatrix} \diagup N(C_7H_7) \cdot CS \cdot NH \cdot C_3H_5 \\ \diagdown NH \cdot C_7H_7 \end{smallmatrix}$	—	99
„ „	Phenyl	$C_2H_4[N(C_7H_7) \cdot CS \cdot NHPh]_2$	178	—
„ „	<i>o</i> -Tolyl	$C_2H_4 \begin{smallmatrix} \diagup N(C_7H_7) \cdot CS \cdot NH \cdot C_7H_7 \\ \diagdown NH \cdot C_7H_7 \end{smallmatrix}$	—	176
„ „	<i>m</i> -Tolyl	$C_2H_4 \begin{smallmatrix} \diagup N(C_7H_7) \cdot CS \cdot NH \cdot C_7H_7 \\ \diagdown NH \cdot C_7H_7 \end{smallmatrix}$	—	170
„ „	<i>p</i> -Tolyl	$C_2H_4[N(C_7H_7) \cdot CS \cdot NH \cdot C_7H_7]_2$	187	—
Ethylene- <i>p</i> -toluidine.	Allyl	$C_2H_4[N(C_7H_7) \cdot CS \cdot NH \cdot C_3H_5]_2$	133	—
„ „	Phenyl	$C_2H_4[N(C_7H_7) \cdot CS \cdot NH]_2$	195	—
„ „	<i>m</i> -Chlorophenyl	$C_2H_4[N(C_7H_7) \cdot CS \cdot NH \cdot C_6H_4Cl]_2$	180	—
„ „	<i>o</i> -Tolyl	$C_2H_4[N(C_7H_7) \cdot CS \cdot NH \cdot C_7H_7]_2$	202	—
„ „	<i>m</i> -Tolyl	$C_2H_4 \begin{smallmatrix} \diagup N(C_7H_7) \cdot CS \cdot NH \cdot C_7H_7 \\ \diagdown NH \cdot C_7H_7 \end{smallmatrix}$	—	179
„ „	<i>p</i> -Tolyl	$C_2H_4[N(C_7H_7) \cdot CS \cdot NH \cdot C_7H_7]_2$	178	—

with benzene as solvent, gave a magnitude of 431, the theoretical value being 410. On treatment for two and a half hours with freshly-precipitated mercuric oxide in a sealed tube at 130—140°, with alcohol as solvent, a small amount of a crystalline substance was obtained, melting at 208°; from analogy with a similar compound, described later, this is in all probability the corresponding dicarbamide derivative.

In addition to the compound melting at 165° a very small amount of a second substance was obtained, melting in the neighbourhood of 128°. This is rather more soluble in solvents than the dithiocarbamide derivative but it was not found possible to isolate it in a state of purity. An analysis shows it to be a mixture of the dithiocarbamide derivative, with an asymmetrical compound resulting from the union of 1 molecule of ethyleneaniline and 1 of the thiocarbimide.

0.2870 gave 0.6985 CO₂ and 0.1766 H₂O. C = 66.39; H = 6.8.

0.3110 „ 37 c.c. moist nitrogen at 20° and 744 mm. N = 13.32.

0.1596 „ 0.1480 BaSO₄. S = 12.7.

C₁₈H₂₁N₃S requires C = 69.45; H = 6.75; N = 13.5; S = 10.28 per cent.

It is interesting to notice that both the symmetrical and asym-

metrical compounds contain almost the same percentage of nitrogen, and consequently the estimation of that element present confirms the supposition that the substance melting at 128° is a mixture of the two derivatives.

Ethyleneaniline and *phenylthiocarbimide* interact together quite readily at 100° , giving a substance only very slightly soluble in boiling alcohol, but moderately in boiling benzene, toluene, or amyl alcohol. Either of these solvents on cooling deposits the dithiocarbamide derivative in needle-shaped crystals melting at 184° .

0.2158 gave 0.5486 CO_2 and 0.1160 H_2O . $\text{C} = 69.35$; $\text{H} = 6.01$.

0.1364 „ 13.2 c.c. moist nitrogen at 17° and 764 mm. $\text{N} = 11.29$.

$\text{C}_{28}\text{H}_{26}\text{N}_4\text{S}_2$ requires $\text{C} = 69.70$; $\text{H} = 5.39$; $\text{N} = 11.61$ per cent.

When this compound is heated with alcohol and mercuric oxide in a sealed tube at 140° for three hours, a small amount of a crystalline substance is obtained, which on recrystallisation from alcohol melts sharply at 215° .

0.1608 gave 16.8 c.c. moist nitrogen at 18° and 750 mm. $\text{N} = 11.91$.

$\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_2$ requires $\text{N} = 12.44$ per cent.

That this substance was the substituted dicarbamide corresponding to the dithiocarbamide derivative was confirmed by its synthesis from ethyleneaniline and phenylcarbimide.

These two substances when heated together at 100° readily combined, giving a crystalline compound which, after recrystallisation from alcohol, melted at 215 — 216° .

0.3100 gave 0.8455 CO_2 and 0.1657 H_2O . $\text{C} = 74.37$; $\text{H} = 5.93$.

0.2230 „ 23.4 c.c. moist nitrogen at 15° and 766 mm. $\text{N} = 12.39$.

$\text{C}_{28}\text{H}_{25}\text{O}_2\text{N}_4$ requires $\text{C} = 74.66$; $\text{H} = 5.77$; $\text{N} = 12.44$ per cent.

Ethyleneaniline and o-Tolylthiocarbimide.—As in the previous case, the two compounds interact at 100° ; the product, a dithiocarbamide derivative, is very slightly soluble in boiling alcohol, benzene, or acetone, but may be recrystallised from boiling toluene, amyl alcohol, or nitrobenzene. From either of these solvents it separates in needles melting at 179° .

0.2010 gave 0.5168 CO_2 and 0.1196 H_2O . $\text{C} = 70.14$; $\text{H} = 6.65$.

0.2478 „ 23 c.c. moist nitrogen at 20° and 766 mm. $\text{N} = 10.70$.

$\text{C}_{30}\text{H}_{30}\text{N}_4\text{S}_2$ requires $\text{C} = 70.58$; $\text{H} = 5.88$; $\text{N} = 10.97$ per cent.

Ethyleneaniline and m-Tolylthiocarbimide.—The reaction takes place quite readily at 100° , and the product, after washing with cold alcohol, may be recrystallised from boiling acetone, when needle-shaped crystals melting at 185° are obtained. In this case, the

position of the substituent methyl group in the thiocarbimide appears to have modified the reaction, analysis showing the compound to be undoubtedly formed by the union of one molecule of ethylene-aniline and one of the thiocarbimide, although excess of the latter was employed in the preparation.

0.2634 gave 0.7064 CO_2 and 0.1452 H_2O . $\text{C} = 73.13$; $\text{H} = 6.12$.

$\text{C}_{22}\text{H}_{23}\text{N}_3\text{S}$ requires $\text{C} = 73.13$; $\text{H} = 6.37$ per cent.

Ethyleneaniline and p-Tolylthiocarbimide.—One molecule of ethylene-aniline and two molecules of the thiocarbimide readily unite under the conditions previously mentioned, with the formation of a dithiocarbamide which is only slightly soluble in alcohol, but may be recrystallised from benzene, toluene, or amyl alcohol, and is obtained from either of these solvents in colourless crystals melting at 190° .

0.2182 gave 0.5590 CO_2 and 0.1281 H_2O . $\text{C} = 69.89$; $\text{H} = 6.52$.

0.1067 „ 10.4 c.c. moist nitrogen at 19° and 746 mm.. $\text{N} = 10.99$.

$\text{C}_{30}\text{H}_{30}\text{N}_4\text{S}_2$ requires $\text{C} = 70.58$; $\text{H} = 5.88$; $\text{N} = 10.97$ per cent.

Ethylene-o-toluidine and Thiocarbimides.

The position of the substituent methyl group in the ethylene-toluidine has a very marked effect on the reaction which takes place.

In the case of allyl- and o-tolyl-thiocarbimides it was found quite impossible to isolate any compound in a state of purity, the yields obtained being very small and the crystals having very indefinite melting points, but little improved by recrystallisation.

In the case of phenyl-, m-tolyl-, and p-tolyl-thiocarbimides the reagents had to be heated for several hours before crystals separated, and some difficulty was experienced in their purification. Analysis showed in each instance that one molecule of ethylenetoluidine had united with one of thiocarbimide to form the asymmetrical thiocarbamide derivative.

Ethylene-o-toluidine and Phenylthiocarbimide.—The compound formed is only slightly soluble in benzene, alcohol, or acetone, but more so in toluene and amyl alcohol, from which solvents crystals are obtained melting at 150° .

0.3195 gave 0.8546 CO_2 and 0.1918 H_2O . $\text{C} = 72.94$; $\text{H} = 6.6$.

$\text{C}_{23}\text{H}_{25}\text{N}_3\text{S}$ requires $\text{C} = 73.6$; $\text{H} = 6.6$ per cent.

The compound from *ethylene-o-toluidine* and m-tolylthiocarbimide yields needle-shaped crystals from acetone, melting at 157° .

0.3368 gave 0.9252 CO_2 and 0.2125 H_2O . $\text{C} = 74.91$; $\text{H} = 7.01$.

$\text{C}_{24}\text{H}_{27}\text{N}_3\text{S}$ requires $\text{C} = 74.03$; $\text{H} = 6.94$ per cent.

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Ethylene-o-toluidine and p-Tolylthiocarbimide.—The crystalline product is readily soluble in alcohol or acetone, and when recrystallised from these solvents melts at 119°.

0.2470 gave 0.6656 CO₂ and 0.1554 H₂O. C = 73.48; H = 6.99.

C₂₄H₂₇N₃S requires C = 74.03; H = 6.94 per cent.

Ethylene-m-toluidine and Allylthiocarbimide.—The reaction between the two substances did not take place at all readily even after prolonged heating. At the end of twelve hours, a viscous mass was obtained which, on treatment with ether, gave a small amount of a crystalline substance.

Since this substance was very soluble in the ordinary organic solvents, considerable difficulty was experienced in its purification. When recrystallised from benzene, it melted at 97—99°, and was obviously not quite pure. Subsequent attempts to obtain it in a purer condition were unsuccessful. The analysis showed that one molecule of ethylenetoluidine had united with one molecule of thiocarbimide, the discrepancy in the proportion of carbon being probably due to contamination with a little ethylenetoluidine.

0.2022 gave 0.5377 CO₂ and 0.1357 H₂O. C = 72.51; H = 7.45.

C₂₀H₂₅N₃S requires C = 70.79; H = 7.37 per cent.

Ethylene-m-toluidine and Phenylthiocarbimide.—Interaction took place readily between the two substances, the product being soluble in boiling acetone. On cooling, needle-shaped crystals of the dithiocarbamide derivative were deposited, melting at 178°.

0.2046 gave 0.5246 CO₂ and 0.1140 H₂O. C = 69.92; H = 6.10.

C₃₀H₃₀N₄S₂ requires C = 70.58; H = 5.8 per cent.

Ethylene-m-toluidine and o-Tolylthiocarbimide.—The interaction between these two substances only takes place slowly, and eight hours' heating was required for its completion. The crystals obtained were only slightly soluble in benzene, and on recrystallising from acetone melted at 176°. The product was the asymmetrical thiocarbamide derivative.

0.2475 gave 0.6790 CO₂ and 0.1440 H₂O. C = 74.81; H = 6.46.

C₂₄H₂₇N₃S requires C = 74.03; H = 6.94 per cent.

Ethylene-m-toluidine and m-Tolylthiocarbimide.—One molecule of each of these substances combines to form the asymmetrical thiocarbamide derivative, which may be recrystallised from boiling acetone, the crystals thus obtained melting sharply at 170°.

0.3007 gave 0.8085 CO₂ and 0.1746 H₂O. C = 73.32; H = 6.45.

C₂₄H₂₇N₃S requires C = 74.03; H = 6.94 per cent.

Ethylene-m-toluidine and p-Tolylthiocarbimide.—This interaction takes place easily and the product is slightly soluble in benzene, but may readily be recrystallised from acetone. The symmetrical dithiocarbamide derivative thus obtained melts at 187°.

0.2614 gave 0.6822 CO₂ and 0.1476 H₂O. C = 71.16; H = 6.25.

C₂₂H₃₄N₄S₂ requires C = 71.37; H = 6.31 per cent.

Ethylene-p-toluidine and Allylthiocarbimide.—The interaction occurs fairly readily, giving a good yield of the dithiocarbamide derivative, which is moderately soluble in alcohol, but is best recrystallised from acetone, this solvent depositing crystals melting at 133°.

0.1797 gave 0.4377 CO₂ and 0.1132 H₂O. C = 66.42; H = 6.9.

C₂₄H₃₀N₄S₂ requires C = 65.75; H = 6.84 per cent.

Ethylene-p-toluidine and Phenylthiocarbimide.—Interaction readily takes place between 1 molecule of the ethylenetoluidine and 2 molecules of phenylthiocarbimide, giving the symmetrical dithiocarbamide which is slightly soluble in benzene and toluene, but more so in acetone; the crystals obtained from either solvent melt at 195°.

0.2240 gave 0.5740 CO₂ and 0.1174 H₂O. C = 69.90; H = 6.00.

0.2532 „ 25 c.c. moist nitrogen at 18° and 760 mm. N = 11.4.

C₃₀H₃₀N₄S₂ requires C = 70.58; H = 5.8; N = 10.98 per cent.

Ethylene-p-toluidine and m-chlorophenylthiocarbimide interact, giving a small yield of a crystalline compound which, when recrystallised from acetone, melts sharply at 180°.

Unlike the corresponding derivative from ethylene-*p*-toluidine and *m*-tolylthiocarbimide it was found that 2 molecules of thiocarbimide had united with one of the base to form a symmetrical dithiocarbamide derivative, but in spite of the usual criteria of purity it appears to be contaminated with a little of the asymmetrical compound, which is richer in carbon. The nitrogen percentage is approximately the same in both compounds, and an estimation of this element strengthens this supposition.

0.3230 gave 0.7504 CO₂ and 0.1525 H₂O. C = 63.3; H = 5.2.

0.3380 „ 28.2 c.c. moist nitrogen at 17° and 762 mm. N = 9.68.

C₃₀H₂₈N₄S₂Cl₂ requires C = 62.17; H = 4.83; N = 9.66.

C₂₃H₂₄N₃SCl requires C = 67.39; H = 5.86; N = 10.25 per cent.

Ethylene-p-toluidine and o-tolylthiocarbimide interact readily and furnish a good yield of the dithiocarbamide derivative. This compound is practically insoluble in alcohol, amyl alcohol, benzene, and toluene, but may be crystallised from nitrobenzene and melts at 202°.

0.1971 gave 0.5097 CO_2 and 0.1144 H_2O . $\text{C} = 70.52$; $\text{H} = 6.4$.

0.1934 „ 17.2 c.c. moist nitrogen at 19° and 766 mm. $\text{N} = 10.30$.

$\text{C}_{32}\text{H}_{34}\text{N}_4\text{S}_2$ requires $\text{C} = 71.37$; $\text{H} = 6.31$; $\text{N} = 10.40$ per cent.

Ethylene-p-toluidine and m-Tolylthiocarbimide.—The product in this case consists of the asymmetrical thiocarbamide derivative, which may be recrystallised from acetone, when it is obtained in the form of white, silky crystals melting at 179° .

It is interesting to notice the influence of the methyl group in the thiocarbimide, the analogous compounds formed from *o*- and *p*-tolylthiocarbimides consisting of the dithiocarbamide derivatives.

0.2898 gave 0.7804 CO_2 and 0.1676 H_2O . $\text{C} = 73.43$; $\text{H} = 6.42$.

0.2624 „ 0.7070 CO_2 „ 0.1630 H_2O . $\text{C} = 73.47$; $\text{H} = 6.90$.

$\text{C}_{24}\text{H}_{27}\text{N}_3\text{S}$ requires $\text{C} = 74.03$; $\text{H} = 6.94$ per cent.

Ethylene-p-toluidine and p-Tolylthiocarbimide.—Combination of 1 molecule of ethylene-*p*-toluidine with two of thiocarbimide readily takes place with formation of the symmetrical dithiocarbamide, a substance which crystallises from acetone in feathery needles melting at 178° , but is only slightly soluble in alcohol and benzene.

0.2768 gave 0.7224 CO_2 and 0.1524 H_2O . $\text{C} = 71.53$; $\text{H} = 6.11$.

$\text{C}_{32}\text{H}_{34}\text{N}_4\text{S}_2$ requires $\text{C} = 71.37$; $\text{H} = 6.31$ per cent.

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