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The Reactions of *N, N*-Dimethylbenzamide Diethylmercaptole

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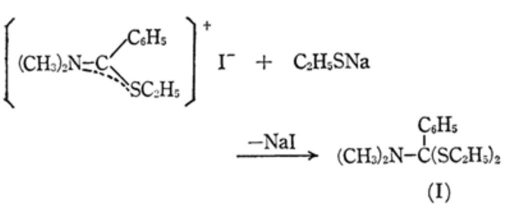
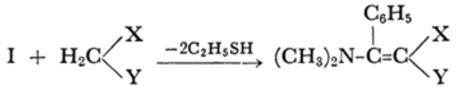
The reactions of *N, N*-dimethylbenzamide diethylmercaptole with active methylene compounds, amines, hydrazines, benzaldoxime, benzhydroxamic acid and heavy metal salts have been studied. Active methylene compounds, hydroxylamine, hydrazine and phenylhydrazine were found to react with *N, N*-dimethylbenzamide diethylmercaptole to give the corresponding α-dimethylaminobenzylidene derivatives by eliminating ethyl mercaptan. In addition, such heterocyclic compounds as 2-phenylimidazoline, 2-phenyloxazoline and 2, 5-diphenyl-1, 3, 4-oxadiazole were derived from *N, N*-dimethylbenzamide diethylmercaptole by cyclization reactions with ethylenediamine, 2-aminoethanol and benzoylhydrazine respectively. Further, it was found that *N, N*-dimethylbenzamide diethylmercaptole reacted with benzaldoxime and benzhydroxamic acid to give the dehydrated products benzonitrile and phenyl isocyanate respectively. Finally, it was established that heavy metal salts, such as mercuric oxide, mercuric cyanide and silver cyanide, reacted with *N, N*-dimethylbenzamide diethylmercaptole to liberate heavy metal mercaptides, thus giving *N, N*-dimethylbenzamide, *N, N*-dimethylbenzamide dicyanide and *N, N*-dimethylbenzamide ethylmercaptocyanide respectively.

It was reported in a preceding paper[1] that *N, N*-dimethylbenzamide methylethylmercaptole had been derived from *N, N*-dimethyl-*S*-methylthiobenzamide iodide and sodium ethylmercaptide. In the present experiment, the reactions of *N, N*-dimethylbenzamide diethylmercaptole (I) with active methylene compounds, amines, hydrazines, benzaldoxime, benzhydroxamic acid and heavy metal salts were investigated.



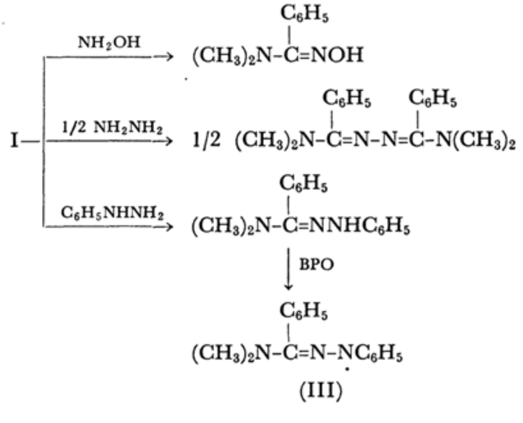
(I)

In the first place, it was found that the amide mercaptole (I) reacted with active methylene compounds to give the condensation products, i. e., α-dimethylaminobenzylidene derivatives (II) of the active methylene compounds, in fairly good yields, along with ethyl mercaptan. For example, malonitrile easily reacted with the amide mercaptole (I) at room temperature, with the evolution of ethyl mercaptan, and gave α-dimethylaminobenzylidene malonitrile (IIa) in a 71% yield; on the other hand, this compound could not be obtained from *N, N*-dimethyl-*S*-methylthiobenzamide iodide by the method mentioned in the previous paper.[1]



(IIa) X, Y = C≡N
(IIb) X, Y = C≡N, $CONH_2$
(IIc) X, Y = H, NO_2

Next, it was established that hydroxylamine, hydrazine and phenylhydrazine easily reacted with the amide mercaptole (I), resulting in the formation of the corresponding condensation products, i. e., *N, N*-dimethylbenzamidoxime, *N, N*-dimethylbenzamidazine and *N, N*-dimethylbenzamide phenylhydrazone respectively, in good yields. The *N, N*-dimethylbenzamide phenylhydrazone thus obtained was a red-brown oil which gradually turned dark-violet when it was exposed to the air. The electron-spin-resonance spectrum of the deep green oil which resulted from the treatment of *N, N*-dimethylbenzamide phenylhydrazone with



(III)

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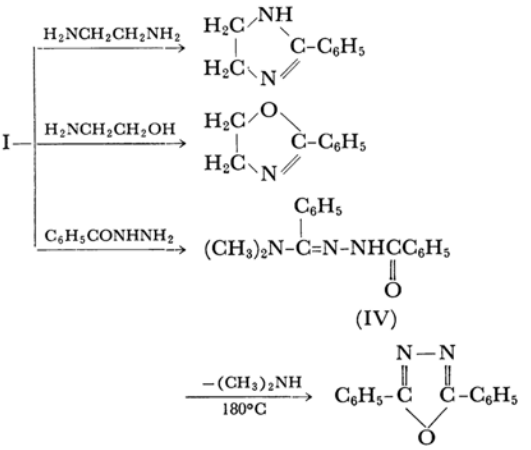
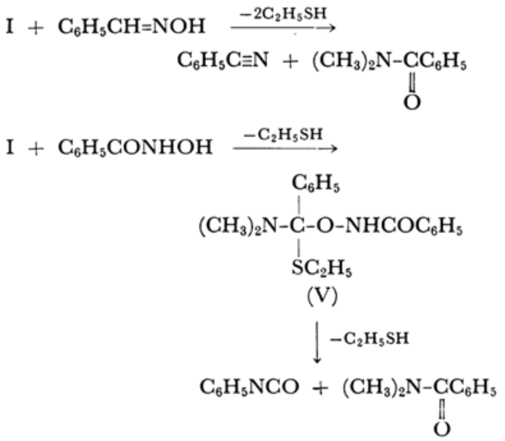
[1] T. Mukaiyama, T. Yamaguchi and H. Nohira, This Bulletin, **38**, 2107 (1965).

benzoyl peroxide in benzene showed seven equally-spaced lines. This result would indicate that a stable free radical with a hydrazyl structure (III) exists in the above-mentioned oily substance.

When *N, N*-dimethylbenzamide diethylmercaptole (I) was treated with bifunctional active hydrogen compounds, such as ethylenediamine and 2-aminoethanol, heterocyclic compounds, i. e., 2-phenylimidazoline and 2-phenyloxazoline respectively, were given in good yields by means of the elimination of ethyl mercaptan and dimethylamine. In addition, the treatment of the amide mercaptole (I) with benzoylhydrazine in refluxing ethyl acetate gave an oily product which, on heating at 180°C, readily solidified to give 2, 5-diphenyl-1, 3, 4-oxadiazole in a 77.5% yield. The initially-obtained oily substance may be identified as *N, N*-dimethylbenzamide benzoylhydrazone (IV) because its infrared spectrum shows absorption bands at 3265 (NH), 2940 (CH_3), 1665 (C=O) and, 1640 cm^{-1} (C=N).



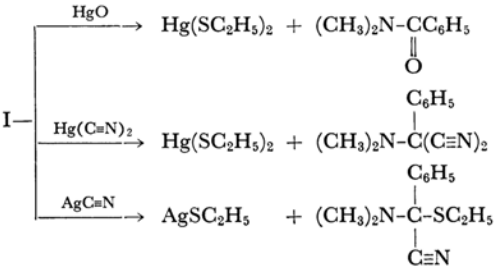
In the next place, since the amide mercaptole (I) is very easily hydrolyzed to *N, N*-dimethylbenzamide and ethyl mercaptan, intramolecular dehydration reactions of benzaldoxime and benzhydroxamic acid by means of the amide mercaptole (I) were attempted. Benzaldoxime reacted with the amide mercaptole (I) to give, as expected, benzonitrile in a good yield, together with *N, N*-dimethylbenzamide and ethyl mercaptan. On the other hand, when benzhydroxamic acid was mixed with the amide mercaptole (I), a vigorous evolution of ethyl mercaptan was observed; after this gas evolution had been ceased, a red-brown oil was obtained. This oily substance decomposed, upon being heated at 140—150°C, to yield phenyl isocyanate and *N, N*-dimethylbenzamide, while ethyl mercaptan was eliminated. The structure of the intermediate oil seems to be V; its infrared spectrum shows main absorption bands at 3250 (NH), 2915 (CH), 1620 (C=O) and 1510 cm^{-1} (CH).



$$\mathrm{I} + C_6H_5CH{=}NOH \xrightarrow{-2C_2H_5SH} C_6H_5C{\equiv}N + (CH_3)_2N\text{-}\underset{\underset{O}{\|}}{C}C_6H_5$$

$$\mathrm{I} + C_6H_5CONHOH \xrightarrow{-C_2H_5SH} (CH_3)_2N\text{-}\underset{SC_2H_5}{\overset{C_6H_5}{C}}\text{-}O\text{-}NHCOC_6H_5 \ \text{(V)} \xrightarrow{-C_2H_5SH} C_6H_5NCO + (CH_3)_2N\text{-}\underset{\underset{O}{\|}}{C}C_6H_5$$

Since some of heavy metal salts can easily be converted to heavy metal mercaptides by treating them with mercaptans, reactions of the amide mercaptole (I) with heavy metal salts, such as mercuric oxide, mercuric cyanide and silver cyanide, were attempted. When mercuric oxide and mercuric cyanide were treated with the amide mercaptole (I), *N, N*-dimethylbenzamide and *N, N*-dimethylbenzamide dicyanide respectively resulted in good yields, while mercury ethylmercaptide was eliminated. In a similar fashion, the reaction of silver cyanide with the amide mercaptole (I) gave silver ethyl mercaptide and *N, N*-dimethylbenzamide ethylmercaptocyanide in fairly good yields.



$$\mathrm{I} \xrightarrow{HgO} Hg(SC_2H_5)_2 + (CH_3)_2N\text{-}\underset{\underset{O}{\|}}{C}C_6H_5$$

$$\mathrm{I} \xrightarrow{Hg(C\equiv N)_2} Hg(SC_2H_5)_2 + (CH_3)_2N\text{-}\overset{C_6H_5}{C}(C{\equiv}N)_2$$

$$\mathrm{I} \xrightarrow{AgC\equiv N} AgSC_2H_5 + (CH_3)_2N\text{-}\underset{C\equiv N}{\overset{C_6H_5}{C}}\text{-}SC_2H_5$$

Further, it was established that the amide mercaptole (I) reacted with lead tetraacetate to give lead acetate, diethyl disulfide, acetic anhydride and *N, N*-dimethylbenzamide in good yields.

$$\mathrm{I} + Pb(OCOCH_3)_4 \rightarrow Pb(OCOCH_3)_2 + CH_3COOCOCH_3 + C_2H_5SSC_2H_5 + (CH_3)_2NCOC_6H_5$$

These results showed that the amide mercaptole (I) was oxidized to *N, N*-dimethylbenzamide and diethyl disulfide, while lead tetraacetate was reduced to lead acetate. In the course of this oxidation-reduction reaction, acetic anhydride was produced in a good yield. The oxidation reactions of amide mercaptoles by means of other oxidizing reagents are now being investigated.

Experimental[2]

N, N-Dimethylbenzamide Diethylmercaptole (I). —A suspension of 64 g. (0.2 mol.) of *N, N*-dimethylbenzamide-*S*-ethylthiobenzamide iodide, prepared from *N, N*-dimethylthiobenzamide and ethyl iodide, and 17 g. (0.2 mol.) of sodium ethylmercaptide in dry ether (300 ml.) was stirred at room temperature for 3 hr. After the white precipitate of sodium iodide had been filtered off, the filtrate was concentrated; the distillation of the residual liquid gave 31 g. (63.5%) of *N, N*-dimethylbenzamide diethylmercaptole (I). B. p. 105—109°C/0.2 mmHg, n_D^{16} 1.5732; IR; 2950(s), 2850(s), 2760(m), 1480(m), 1445(s), 1260(m), 1010(s), 790(s), 730(s) and 700 cm^{-1}(s).

Found: C, 63.27; H, 8.20; N, 5.96. Calcd. for $C_{13}H_{21}NS_2$: C, 63.15; H, 8.19; N, 5.45%.

N, N-Dimethylbenzamide diethylmercaptole (I) is a pale yellow oil with a mercaptan odor; it turns red-brown after standing for a few days.

The Reaction of the Amide Mercaptole (I) with Malonitrile.—A solution of 2.50 g. (0.01 mol.) of the amide mercaptole (I) and 0.66 g. (0.01 mol.) of malonitrile in dry ether (30 ml.) was stirred at room temperature. The reaction soon started, with the evolution of ethyl mercaptan, and a white precipitate was separated from the solution. After the stirring had been continued for 2 hr., the white precipitate was filtered and recrystallized from 95% ethanol. Yield IIa, 1.40 g. (71%); m. p. 120—121°C.

Found: C, 73.14; H, 5.51; N, 21.28. Calcd. for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.38%.

The infrared spectrum of this compound showed the absorption band at 2180 cm^{-1} assigned to the C≡N bond.

The Reaction of the Amide Mercaptole (I) with Cyanoacetamide.—When a mixture of 2.50 g. (0.01 mol.) of the amide mercaptole (I) and 0.85 g. (0.01 mol.) of cyanoacetamide was heated at 115°C, the evolution of ethyl mercaptan was observed. After 5 minutes' heating, the reaction mixture was cooled and triturated with dry ether. Then the ether was evaporated and the resulting solid was recrystallized from 95% ethanol. Yield (IIb), 0.7 g. (32.5%); m. p. 163—164°C.

Found: C, 67.06; H, 5.99; N, 19.45. Calcd. for $C_{12}H_{13}N_3O$: C, 66.95; H, 6.09; N, 19.52%.

The infrared spectrum of this compound showed absorption bands at 3370, 2160 and 1640 cm^{-1}.

The Reaction of the Amide Mercaptole (I) with Nitromethane.—A solution of 2.50 g. (0.01 mol.) of the amide mercaptole (I) and 0.65 g. (0.01 mol.) of nitromethane in benzene (10 ml.) was refluxed for an hour. After the benzene had been removed in vacuo, the resulting solid was recrystallized from benzene (or ethanol). Yield IIc, 1.00 g. (52%); m. p. 128°C. This material showed no depression in a mixed melting point determination with an authentic sample prepared by the previously reported method.[1]

The Reaction of the Amide Mercaptole (I) with Hydroxylamine.—Hydroxylamine was prepared from hydroxylamine hydrochloride by the method described in the literature.[3] M. p. 31—33°C. A benzene solution of 1.20 g. (0.005 mol.) of the amide mercaptole (I) and 0.175 g. (0.005 mol.) of hydroxylamine was refluxed for 2 hr. After this mixture had cooled, the solvent was removed in vacuo and the resulting *N, N*-dimethylbenzamidoxime was recrystallized from benzene. Yield, 0.82 g. (92%); m. p. 123—124°C.

Found: C, 65.76; H, 7.42; N, 16.89. Calcd. for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06%.

The Reaction of the Amide Mercaptole (I) with Hydrazine.—Anhydrous hydrazine was prepared by the dehydration of hydrazine hydrate with sodium hydroxide. B. p. 114°C. A solution of 2.45 g. (0.01 mol.) of the amide mercaptole (I) and 0.16 g. (0.005 mol.) of hydrazine in dry benzene (20 ml.) was refluxed for 2 hr. After the benzene had been removed in vacuo, the resulting white solid was recrystallized from ethanol. Yield, 1.00 g. (68%); m. p. 137—138°C.

Found: C, 73.54; H, 7.47; N, 18.85. Calcd. for $C_{18}H_{22}N_4$: C, 73.43; H, 7.53; N, 19.03%.

The Reaction of the Amide Mercaptole (I) with Phenylhydrazine.—To a solution of the amide mercaptole (I) (2.50 g., 0.01 mol.) in dry benzene (20 ml.), there was added a solution of phenylhydrazine (1.08 g., 0.01 mol.) in dry benzene (10 ml.) under a nitrogen atmosphere. After it had been refluxed for 2 hr., the reaction mixture was concentrated and distilled in vacuo under nitrogen. Yield, 1.71 g. (71.5%); b. p. 127—129°C/0.03 mmHg.

Found: C, 73.83; H, 7.06; N, 17.36. Calcd. for $C_{15}H_{17}N_3$: C, 75.28; H, 7.16; N, 17.56%.

To a solution of 0.50 g. of *N, N*-dimethylbenzamide phenylhydrazone in dry benzene (15 ml.) there was added, drop by drop, a solution of 0.25 g. of benzoyl peroxide in dry benzene (10 ml.) under a nitrogen atmosphere. The dark-colored reaction mixture was stirred for an additional 30 min., and then the benzene was removed in vacuo at room temperature. The electron-spin-resonance spectrum of the resulting deep-green oil was recorded in the benzene solution.

The Preparation of 2-Phenylimidazoline and of 2-Phenyloxazoline.—A solution of 1.25 g. (0.005 mol.) of the amide mercaptole (I) and 0.30 g. (0.005 mol.) of anhydrous ethylenediamine in dry benzene (20 ml.) was refluxed for 3 hr. Then the benzene was removed under reduced pressure, and the resulting 2-phenylimidazoline was recrystallized from ethanol (or benzene). Yield, 0.70 g. (96%); m. p. 100—101°C (lit.[4] 101°C). A mixed melting point determination with an authentic sample showed no depression.

In a similar way, 2-phenyloxazoline was obtained in a 67% yield (b. p. 125—127°C/17 mmHg) when the amide mercaptole (I) and 2-aminoethanol were reacted in refluxing chloroform for 3 hr.

Found.: C, 73.00; H, 6.76; N, 9.47. Calcd. for C_9H_9NO: C, 73.45; H, 6.61; N, 9.52%.

The Reaction of the Amide Mercaptole (I) with Benzoylhydrazine.—A solution of 2.60 g. (0.01 mol.) of the amide mercaptole (I) and 1.36 g. (0.01 mol.) of benzoylhydrazine in 40 ml. of ethyl acetate was refluxed for 3 hr., and then the solvent was removed under reduced pressure. The resulting yellow oil was, in situ, heated to 180°C for a while; after it had cooled, it solidified to give 2, 5-diphenyl-1, 3, 4-oxadiazole (1.72 g.;

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[2] All melting points and boiling points are uncorrected.

[3] H. S. Booths, "Inorganic Synthesis," Vol. I, McGraw-Hill Book Co. New York (1939), p. 87.

[4] G. Forrsel, *Ber.*, **25**, 2135 (1892).

77.5%), which was then recrystallized from absolute ethanol. M. p. 136—137°C)lit.5) 135—136°C).

Found: C, 75.61; H, 5.02; N, 12.41. Calcd. for $C_{14}H_{10}N_2O$: C, 75.65; H, 4.54; N, 12.61%.

The Reaction of the Amide Mercaptole (I) with Benzaldoxime.—A solution of 2.60 g. (0.01 mol.) of the amide mercaptole (I) and 1.21 g. (0.01 mol.) of *syn*-benzaldoxime in dry benzene (25 ml.) was refluxed for an hour. After the benzene had been removed, the residual liquid was distilled in vacuo to give 0.66 g. (67.5%) of benzonitrile (b. p. 88—93°C/22 mmHg), together with *N, N*-dimethylbenzamide (1.19 g., 80%; b. p. 93—98°C/1.0 mmHg). They were identified by comparing their infrared spectra with those of authentic samples.

The Reaction of the Amide Mercaptole (I) with Benzhydroxamic Acid.—When 2.60 g. (0.01 mol.) of the amide mercaptole (I) was mixed with 1.37 g. (0.01 mol.) of benzhydroxamic acid, an exothermic reaction soon took place and ethyl mercaptan was evolved violently. After the gas evolution had ceased, the resulting red-brown oil was, in situ, heated at 140—155°C; then it was distilled under reduced pressure to give 0.68 g. (57.5%) of phenyl isocyanate and 1.23 g. (82%) of *N, N*-dimethylbenzamide.

The Reaction of the Amide Mercaptole (I) with Mercuric Oxide.—Into a suspension of 2.16 g. (0.01 mol.) of meruric oxide in acetonitrile (25 ml.), there was added a solution of 2.60 g. (0.01 mol.) of the amide mercaptole (I) in acetonitrile (10 ml.). After the reaction mixture had then been stirred at room temperature for 30 min., it was heated at 50°C for an additional 30 min., cooled, and filtered to remove a white percipitate. After the filtrate had been concentrated, the resulting solid part was filtered, washed, and combined with the initial precipitate; this gave 1.20 g. (46%) of mercury ethylmercaptide (recrystallized from ethanol; m. p. 76—78°C; lit.6) 76.5°C). The filtrate was concentrated and distilled to give 0.90 g. (60%) of *N, N*-dimethylbenzamide, b. p. 145—147°C/34 mmHg.

The Reactions of the Amide Mercaptole (I) with Mercuric Cyanide and Silver Cyanide.—A solution of 2.60 g. (0.01 mol.) of the amide mercaptole (I) in dry tetrahydrofuran (10 ml.) was added to a suspension of 2.52 g. (0.01 mol.) of mercuric cyanide in dry tetrahydrofuran (15 ml.); the mixture was then stirred at room temperature for an hour. After the solvent had been removed in vacuo, the resulting solid was recrystallized from acetonitrile (ca. 10 ml.); filtration gave 0.95 g. (72%) of mercury ethylmercaptide. The filtrate was concentrated and distilled to give 1.18 g. (64%) of *N, N*-dimethylbenzamide dicyanide, b. p. 100—103°C/5 mmHg.

Found: C, 71.44; H, 5.99. Calcd. for $C_{11}H_{11}N_3$: C, 71.33; H, 5.99%.

In a similar way, when silver cyanide was treated with the amide mercaptole (I) in refluxing tetrahydrofuran, pale yellow silver mercaptide was precipitated; this was then filtered off. The distillation of the filtrate gave a 46% yield of *N, N*-dimethylbenzamide ethylmercaptocyanide (b. p. 103—107°C/1.0 mmHg), which showed an infrared spectrum identical with that of the authentic sample derived by the previously-reported method.1)

The Reaction of the Amide Mercaptole (I) with Lead Tetraacetate.—When a solution of 2.60 g. (0.01 mol.) of the amide mercaptole (I) and 4.43 g. (0.01 mol.) of lead tetraacetate in dry benzene (50 ml.) was heated at 60°C, a white precipitate was separated from the solution. After stirring had been continued for 2.5 hr., the white precipitate of lead acetate was filtered and dried. It weighed 2.28 g. (70%). The filtrate was then concentrated and fractionated, giving 0.80 g. (81%) of acetic anhydride (b. p. 65—67°C/57 mmHg), 0.43 g. (70%) of diethyl disulfide (b. p. 74—75°C/45 mmHg) and 1.07 g. (71%) of *N, N*-dimethylbenzamide (b. p. 130—133°C/17 mm Hg). They were identified by means of their infrared spectra.

The authors wish to thank Dr. Kazuo Shimogoshi for his analysis of the ESR spectrum.

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5) E. Günther, *Ann.*, **254**, 64 (1889).
6) A. Gutmann, *Ber.*, **49**, 953 (1916).