234. *Syntheses of Thio-oxamides and Thioamides by Extensions of the Kindler Reaction.*

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Further preparations of substituted thio-oxamides (II) from carbamoylmethyl thiolsulphates (I) are recorded and the reaction is extended to phenoxycarbonylmethyl and ethoxycarbonylmethyl thiolsulphates (III). Thio-oxamides are also obtained by heating chloroacetyl-, dichloroacetyl-, or trichloroacetyl-amines with sulphur and a primary or secondary amine, while benzyl chloride, benzylidene chloride, and benzotrichloride yield thiobenzoamides under the same conditions. Similar reaction of glyoxal, trichloroethylene, or tetrachloroethane with sulphur and an amine affords substituted dithio-oxamides.

Thiolsulphates (IV), prepared from halogenomethyl ketones, react with morpholine to give 4-acyl(thioformyl) derivatives (V) of morpholine.

IN an earlier paper [1] it was shown that monothio-oxamides (II) are formed when carbamoylmethyl thiolsulphates (I) are heated with primary or secondary amines. Some further examples and various extensions and developments of this reaction are now reported.

(I) $R{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}S_2O_3Na$ $\qquad$ $RNH{\cdot}CO{\cdot}CS{\cdot}NR'R''$ (II)

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[1] Milligan and Swan, *J.*, 1959, 2969.

Schiff's bases or diaminomethylene compounds are believed to be intermediates in the Kindler reaction [2] and in these reactions of carbamoylmethyl thiolsulphates. Such compounds should also be formed by reaction of amines with dichloromethylene compounds, so that in the presence of sulphur these might also yield thioamides. When dichloroacetylamines were heated with sulphur and an amine monothio-oxamides were formed, often in very high yield. Thus *o*-dichloroacetamidobenzoic acid, cyclohexylamine, and one atomic proportion of sulphur gave N^{o}-*o*-carboxyphenyl-N^{s}-cyclohexyl(thio-oxamide) (II; R = $HO_2C{\cdot}C_6H_4$, R′ = C_6H_{11}, R″ = H), also obtained by heating the appropriate thiolsulphate (I; R = $HO_2C{\cdot}C_6H_4$) with cyclohexylamine. The corresponding N^{o}-*p*-carboxyphenyl-N^{s}-cyclohexyl(thio-oxamide) was similarly obtained. Dichloroacetanilide, sulphur, and cyclohexylamine, morpholine, or diethylamine gave thio-oxamides in yields greater than 90%. N^{s}-Cyclohexyl-N^{o}-phenyl(thio-oxamide) (II; R = Ph, R′ = C_6H_{11}, R″ = H), 4-(phenyl-α-thio-oxamoyl)morpholine * (II; R = Ph, R′R″ = $CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2$), and N^{s}-diethyl-N^{o}-phenyl(thio-oxamide) (II; R = Ph, R′ = R″ = Et) were thus obtained. The reaction of dichloroacetamide with sulphur and cyclohexylamine gave N^{s}-cyclohexyl(thio-oxamide) (II; R = R′ = H, R″ = C_6H_{11}) in almost quantitative yield, but with morpholine the yield of 4-(α-thio-oxamoyl)morpholine was only 11%. This product was also obtained from morpholine and sodium carbamoylmethyl thiolsulphate (I; R = H).

Dichloroacetic acid, when heated with cyclohexylamine and sulphur, gave only *NN*′-dicyclohexylthiourea in low yield. Presumably decarboxylation here occurs to give dicyclohexylaminomethane, and the methylene group is then oxidised by sulphur to CS. The same thiourea was obtained on heating either methylene chloride or chloroform with sulphur and cyclohexylamine; methylene chloride, sulphur, and benzylamine gave the corresponding *NN*′-dibenzylthiourea but with morpholine the only product isolated was apparently 4-thioformylmorpholine. No crystalline product was obtained from reaction of carbon tetrachloride, sulphur, and amines.

The analogous chloromethyl and trichloromethyl compounds also yielded the same thioamides when heated with sulphur and an amine; the yields from the former were higher when two atomic proportions of sulphur were used. Thus chloroacetanilide, sulphur, and either cyclohexylamine or morpholine gave N^{s}-cyclohexyl-N^{o}-phenyl(thio-oxamide) and 4-(phenyl-α-thio-oxamoyl)morpholine, respectively; the same products were also obtained in fair yield from trichloroacetanilide. Benzyl chloride with two equivalents of sulphur in either cyclohexylamine or morpholine gave *N*-cyclohexyl(thiobenzamide) and thiobenzomorpholide, respectively. These same products were also obtained from *S*-benzylthiouronium chloride, from benzylidene chloride, and from benzotrichloride. The best yields (75—99%) in all these experiments were obtained, as expected, from benzylidene chloride, and this compound also gave rise to *N*-benzyl(thiobenzamide) on being heated with sulphur and benzylamine.

N-Cyclohexyl(thiobenzamide) and thiobenzomorpholide were also prepared by heating the appropriate amine with sulphur and benzaldehyde. In addition, thiobenzomorpholide was obtained on heating benzylideneaniline with morpholine and sulphur. When aqueous glyoxal was heated with sulphur and cyclohexylamine, the expected product, *NN*′-dicyclohexyl(dithio-oxamide) was formed. No crystalline product was obtained when either morpholine or aniline was used in place of cyclohexylamine. Better results were obtained by replacing the glyoxal with trichloroethylene or tetrachloroethane. These new syntheses of dithio-oxamides are somewhat analogous to earlier methods, in which either acetylene [3,4] or a vinyl ether or ester [5] is heated with sulphur and an amine. The synthesis of

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* The nomenclature used is discussed in the previous paper.[1]

[2] King and McMillan, *J. Amer. Chem. Soc.*, 1948, **70**, 4143.

[3] Levesque, U.S.P., 2,525,075/1950; *Chem. Abs.*, 1951, **45**, 2499.

[4] Consonno and Cruto, *Gazzetta*, 1921, **51**, 181.

[5] Levesque, U.S.P., 2,531,283/1950; *Chem. Abs.*, 1951, **45**, 3412.

NN'-diphenyl(dithio-oxamide) by heating tetrabromoethane with aniline in alcoholic alkali, and then heating the unstable product with sulphur, has also been reported.[6]

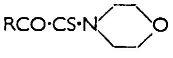
In the reaction of thiolsulphates with amines,[1] only carbamoylmethyl thiolsulphates (I) yielded thio-oxamides when heated with amines, while other thiolsulphates were converted into disulphides. We have now found that sodium phenoxycarbonylmethyl thiolsulphate (III; R = Ph) and sodium ethoxycarbonylmethyl thiolsulphate (III; R = Et) react with cyclohexylamine and also with benzylamine to yield *NN'*-dicyclohexyl- and *NN'*-dibenzyl-(thio-oxamide), respectively. The phenoxy-compound also reacted with aniline to give the *NN'*-diphenyl compound. *NN'*-Dicyclohexyl(thio-oxamide) was also obtained when sodium anilinocarbamoylmethyl thiolsulphate (I; R = PhNH) was heated with cyclohexylamine. In these reactions, the first step may well be replacement of the phenoxy-, ethoxy-, or phenylhydrazino-group by amine, so that the subsequent reaction proceeds through a carbamoylmethyl thiolsulphate. However, a true variant of the thiolsulphate ⟶ thioamide reaction is the synthesis of 4-benzoyl(thioformyl)morpholine (V; R = Ph) from sodium phenacyl thiolsulphate (IV; R = Ph) and morpholine. 4-Acetyl(thioformyl)morpholine (V; R = Me) was prepared similarly from the crude thiolsulphate derived from bromoacetone.

$\mathrm{RO{\cdot}CO{\cdot}CH_2{\cdot}S_2O_3Na}$

(III)

$\mathrm{R{\cdot}CO{\cdot}CH_2{\cdot}S_2O_3Na}$

(IV)



(V)

EXPERIMENTAL

The light petroleum used had b. p. 55—70°. Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory.

N^{O}-p-*Carboxyphenyl*-N^{S}-*cyclohexyl*(*thio-oxamide*).—(i) *p*-Chloroacetamidobenzoic acid and sodium thiosulphate (1 equiv.) were heated under reflux in aqueous 2-methoxyethanol for 30 min. Excess of cyclohexylamine was added and boiling was continued for 5 min. The yellow precipitate was crystallized from ethanol. The *cyclohexylammonium salt* of N^{O}-*p*-carboxyphenyl-N^{S}-cyclohexyl(thio-oxamide) separated as yellow needles, m. p. 228° (Found: C, 62·2; H, 7·7; N, 9·8; S, 7·8. $C_{21}H_{31}N_3O_3S$ requires C, 62·2; H, 7·7; N, 10·4; S, 7·9%). This salt was dissolved in chloroform and shaken with excess of 10% sodium hydroxide solution. Acidification of the aqueous phase gave N^{O}-p-*carboxyphenyl*-N^{S}-*cyclohexyl*(*thio-oxamide*), yellow needles, m. p. 248° (from ethanol) (Found: C, 59·1; H, 6·0; N, 8·7; S, 10·4. $C_{15}H_{18}N_2O_3S$ requires C, 58·8; H, 5·9; N, 9·2; S, 10·5%).

(ii) Crude *p*-dichloroacetamidobenzoic acid (2·2 g., from 2·8 g. of the amine), sulphur (0·28 g.), and cyclohexylamine were heated under reflux for 5 min., and then ethanol was added. The yellow cyclohexylammonium salt of N^{O}-*p*-carboxyphenyl-N^{S}-cyclohexyl(thio-oxamide) (2·34 g., 65% based on *p*-dichloroacetamidobenzoic acid) had m. p. 223° raised to 228° on crystallization from ethyl acetate. The m. p. was undepressed on admixture with a sample prepared by method (i).

N^{O}-o-*Carboxyphenyl*-N^{S}-*cyclohexyl*(*thio-oxamide*).—(i) Anthranilic acid was converted *via* its *N*-chloroacetyl derivative into the corresponding Bunte salt (3 g.) which was heated under reflux with cyclohexylamine (10 ml.) for 5 min., and the mixture poured into a mixture of excess of dilute hydrochloric acid and ethyl acetate. The yellow *cyclohexylammonium salt* (0·25 g.) of N^{O}-*o*-carboxyphenyl-N^{S}-cyclohexyl(thio-oxamide) was crystallized from ethanol. Yellow needles, m. p. 221°, were obtained (Found: C, 62·2; H, 7·6; N, 10·4; S, 8·0. $C_{21}H_{31}N_3O_3S$ requires C, 62·2; H, 7·7; N, 10·4; S, 7·9%). The ethyl acetate layer was extracted several times with 5% sodium hydroxide solution. These extracts slowly deposited yellow needles (1·06 g.), identified as the *sodium salt* of N^{O}-*o*-carboxyphenyl-N^{S}-cyclohexyl(thio-oxamide) (Found: C, 52·8; H, 5·4; N, 8·4; S, 9·5. $C_{15}H_{17}N_2O_3SNa,H_2O$ requires C, 52·0; H, 5·5; N, 8·1; S, 9·3%). Acidification of the alkaline extracts gave N^{O}-o-*carboxyphenyl*-N^{S}-*cyclohexyl*(*thio-oxamide*) (0·73 g.), yellow needles, m. p. 170° after crystallization from carbon tetrachloride–light petroleum. The Lassaigne test showed presence of halogen (Found: C, 54·1; H, 5·3; N, 8·2; S, 9·4. $C_{15}H_{18}N_2O_3S,\frac{1}{4}CCl_4$ requires C, 53·1; H, 5·3; N, 8·1; S, 9·3%).

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[6] Ssabanejew and Prosin, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 233; 1902, **34**, 405.

(ii) *N*-Dichloroacetylanthranilic acid (1·0 g.), sulphur (0·13 g.), and cyclohexylamine (5 ml.) were heated under reflux for 5 min. Ethanol (30 ml.) was added to the cooled mixture; the yellow cyclohexylammonium salt of N^{O}-*o*-carboxyphenyl-N^{S}-cyclohexyl(thio-oxamide) (1·37 g., 84%) had m. p. 218°, undepressed on admixture with a sample prepared by method (i).

Reaction of Dichloroacetanilide with Sulphur and an Amine.—(i) Dichloroacetanilide (1·0 g.), sulphur (0·16 g.), and cyclohexylamine (5 ml.) were heated under reflux for 5 min. N^{S}-Cyclohexyl-N^{O}-phenyl(thio-oxamide),[1] m. p. 130°, was obtained in 93% yield.

(ii) *N*-Phenyl-α-thio-oxamoylmorpholine,[1] m. p. 166°, was obtained in 93% yield by reaction of dichloroacetanilide, sulphur (1 atomic proportion), and morpholine.

(iii) Reaction of dichloroacetanilide (1·0 g.), sulphur (0·16 g.), and diethylamine (5 ml.) in a sealed tube at 150° for 5 min. gave N^{S}-diethyl-N^{O}-phenyl(thio-oxamide) (94% yield), plates (from aqueous ethanol), m. p. 125° (Found: C, 61·2; H, 6·6; N, 11·5; S, 13·8. $C_{12}H_{16}N_2OS$ requires C, 61·0; H, 6·8; N, 11·9; S, 13·6%).

(iv) No thio-oxamide was obtained by reaction of dichloroacetanilide, sulphur, and aniline.

N^{S}-*Cyclohexyl(thio-oxamide)*.—Dichloroacetamide (1·28 g.), sulphur (0·32 g.), and cyclohexylamine (10 ml.) were heated under reflux for 5 min. N^{S}-Cyclohexyl(thio-oxamide) (1·85 g., 99%) crystallized from light petroleum as yellow laths, m. p. and mixed m. p.[1] 108°.

4-(α-*Thio-oxamoyl*)*morpholine*.—(i) Impure sodium carbamoylmethyl thiolsulphate (2·0 g.) and morpholine (10 ml.) were heated under reflux for 5 min. The product (0·5 g.) crystallized from chloroform–light petroleum as pale yellow prisms, m. p. 160° (Found: C, 41·7; H, 5·9; N, 15·4; S, 18·4. $C_6H_{10}N_2O_2S$ requires C, 41·4; H, 5·8; N, 16·1; S, 18·4%).

(ii) By heating a mixture of dichloroacetamide (1·28 g.), sulphur (0·32 g.), and morpholine, 4-(α-thio-oxamoyl)morpholine (0·19 g., 11%) was obtained.

Reaction of Dichloroacetic Acid, Cyclohexylamine, and Sulphur.—Dichloroacetic acid (12·9 g.), sulphur (3·2 g.), and cyclohexylamine (30 ml.) were heated under reflux for 10 min. *NN'*-Dicyclohexylthiourea [7] crystallized from benzene–light petroleum as plates (0·98 g.), m. p. and mixed m. p. 178° after further crystallization from ethanol. Treatment of the product with peracetic acid gave *NN'*-dicyclohexylurea, m. p. 238° (lit.,[8] 229—230°), undepressed on admixture with an authentic sample, m. p. 238°.

Reaction of Methylene Chloride, Sulphur, and an Amine.—(i) Methylene chloride (1·70 g.), sulphur (1·28 g.), and cyclohexylamine (15 ml.) were heated in a sealed tube at 150° for 10 min. The neutral product (3·05 g.) gave *NN'*-dicyclohexylthiourea (0·92 g., 19%) after crystallization from benzene–light petroleum. (ii) Reaction of methylene chloride (2·0 g.), sulphur (1·5 g.), and benzylamine at 150° for 30 min. gave a neutral product (4·97 g.) from which *NN'*-dibenzylthiourea (2·71 g., 45%), m. p. 145° (lit.,[9] 146°) was obtained by crystallization from ethanol.

(iii) Reaction of methylene chloride, sulphur, and morpholine at 150° for 30 min. gave a product which was chromatographed on alumina. Elution with benzene–light petroleum (1 : 1) afforded crystalline material (0·5 g.), m. p. 64° after two crystallizations from water [presumably 4-(thioformyl)morpholine (lit.,[10] m. p. 67·5—68·5°)].

Reaction of Chloroform, Sulphur, and Cyclohexylamine.—(i) Chloroform (2·38 g.), sulphur (1·28 g.), and cyclohexylamine (15 ml.) were heated in a sealed tube for 10 min. The neutral product gave *NN'*-dicyclohexylthiourea (0·52 g., 11%) after crystallization from methanol.

Reaction of Chloroacetanilide, Sulphur, and an Amine.—(i) Chloroacetanilide (2·0 g.), sulphur (0·76 g.), and cyclohexylamine (10 ml.) were heated under reflux for 5 min. The mixture was partitioned between ethyl acetate and water, and the organic phase washed with dilute acid, dried, and evaporated. The residue, N^{S}-cyclohexyl-N^{O}-phenyl(thio-oxamide) (2·60 g., 84%), after crystallization from ethanol had m. p. and mixed m. p.[1] 130°. Addition of hydrochloric acid to the aqueous phase gave *N*-cyclohexyl(phenylcarbamoylmethyl)ammonium chloride, plates, m. p. >200° (from water) (Found: C, 62·4; H, 7·9; N, 10·2. $C_{14}H_{21}ClN_2O$ requires C, 62·6; H, 7·9; N, 10·4%). Neither this salt nor the parent amine gave any thio-oxamide when heated with sulphur and cyclohexylamine.

Reaction of chloroacetanilide, sulphur (1 atomic proportion), and cyclohexylamine as above gave the thio-oxamide in 48% yield.

(ii) Reaction of chloroacetanilide with sulphur (2 atomic proportions) and excess of

[7] Zetzsche and Fredrich, *Ber.*, 1940, **73**, 1114.

[8] Skita and Rolfes, *Ber.*, 1920, **53**, 1248.

[9] Werner, *J.*, 1891, **59**, 396.

[10] King and McMillan, *J. Amer. Chem. Soc.*, 1947, **69**, 1207.

morpholine as in (i) gave *N*-phenyl-α-thio-oxamoylmorpholine (57%), m. p. and mixed m. p. 166° after crystallization from methanol. When only 1 atomic proportion of sulphur was used the yield fell to 44%.

Reaction of Trichloroacetanilide, Sulphur, and an Amine.—(i) Reaction of trichloroacetanilide, sulphur (1 atomic proportion), and cyclohexylamine gave N^S-cyclohexyl-N^O-phenyl(thio-oxamide) in 55% yield.

(ii) *N*-Phenyl-α-thio-oxamoylmorpholine was obtained in 63% yield by reaction of trichloroacetanilide, sulphur (1 atomic proportion) and excess of morpholine.

Reaction of Benzyl Compounds, Sulphur, and an Amine.—(i) Benzyl chloride, sulphur (2 atomic proportions), and cyclohexylamine were heated under reflux for 5 min. *N*-Cyclohexyl-(thiobenzamide), yellow prisms, m. p. 89° (from ethanol), was obtained in 73% yield.

(ii) Reaction of benzyl chloride, sulphur (2 atomic proportions), and morpholine gave a 20% yield of thiobenzomorpholide, prisms, m. p. 137° (from ethanol).

(iii) Reaction of *S*-benzylthiouronium chloride, sulphur (2 atomic proportions), and morpholine gave thiobenzomorpholide in 71% yield. With cyclohexylamine in place of morpholine the yield of *N*-cyclohexyl(thiobenzamide) was 77%.

Reaction of Benzylidene Chloride, Sulphur, and an Amine.—(i) Benzylidene chloride (2·0 g.), sulphur (0·40 g.), and cyclohexylamine (10 ml.) were heated under reflux for 10 min., giving *N*-cyclohexyl(thiobenzamide) (2·7 g., 99%; 70% after crystallization from light petroleum).

(ii) Benzylidene chloride, sulphur (1 atomic proportion), and morpholine were heated; the neutral product gave thiobenzomorpholide (from ethanol) (1·83 g., 75%).

(iii) Reaction of benzylidene chloride, sulphur (1 atomic proportion), and benzylamine gave *N*-benzyl(thiobenzamide), yellow needles (57%), m. p. 87° (lit.,[11] 86°) (from light petroleum).

Reaction of Benzotrichloride, Sulphur, and an Amine.—(i) Benzotrichloride (1·95 g.), sulphur (0·64 g., 2 atomic proportions), and cyclohexylamine (10 ml.) were heated under reflux for 10 min. The neutral product gave *N*-cyclohexyl(thiobenzamide) (1·34 g., 61%) after crystallization from light petroleum.

(ii) With morpholine, thiobenzomorpholide (47% after crystallization from water) was obtained.

Reaction of Benzaldehyde, Sulphur, and an Amine.—(i) Thiobenzomorpholide (73%) was obtained by heating benzaldehyde, sulphur (1 atomic proportion), and excess of morpholine under reflux for 5 min.

(ii) With cyclohexylamine in place of morpholine, cyclohexyl(thiobenzamide) was obtained in 41% yield.

Reaction of N-*Benzylideneaniline, Sulphur, and Morpholine.*—Thiobenzomorpholide (90%) was obtained by heating benzylideneaniline, sulphur (1 atomic proportion), and morpholine under reflux for 10 min.

NN′-*Dicyclohexyl(dithio-oxamide).*—(i) Glyoxal (50%; 5 g.) was diluted with water (20 ml.), and cyclohexylamine was added with cooling. Sulphur (2·5 g.) was stirred in, and the mixture was heated to the b. p., cooled, and then acidified. Crystallization of the precipitate from ethanol gave *NN′*-dicyclohexyl(dithio-oxamide) (4·9 g., 41%), m. p. 150° after crystallization from acetic acid (Levesque [3,5] records m. p. 156—158°; Naylor and Hook [12] m. p. 145—147°) (Found: C, 59·4; H, 8·3; N, 9·3. Calc. for $C_{14}H_{24}N_2S_2$: C, 59·1; H, 8·5; N, 9·9%). Oxidation with peracetic acid gave *NN′*-dicyclohexyloxamide, m. p. and mixed m. p. 273°.

(ii) Trichloroethylene (2·6 g.), sulphur (1·28 g.), and cyclohexylamine (15 ml.) were heated in a sealed tube at 160° for 30 min. *NN′*-Dicyclohexyl(dithio-oxamide) (4·18 g., 74%) crystallized from n-butanol as prisms, m. p. 148°.

(iii) A mixture of tetrachloroethane (3·2 g.), sulphur (1·3 g.) and cyclohexylamine (20 ml.) was heated under reflux for 30 min. *NN′*-Dicyclohexyl(dithio-oxamide) (1·8 g., 65%) had m. p. 148° after one crystallization from ethanol.

4,4′-*Dithio-oxaloylbismorpholine.*—Tetrachloroethane (3·2 g.), sulphur (1·3 g.), and morpholine were heated under reflux for 3 hr. The neutral product (2·9 g.) gave 4,4′-dithio-oxaloylbismorpholine (0·44 g., 10%) as pale yellow prisms, m. p. 255° after crystallization from benzene.

Sodium Phenoxycarbonylmethyl Thiolsulphate.—A mixture of phenyl chloroacetate (15 g.) and sodium thiosulphate pentahydrate (22 g.) in 50% aqueous ethanol (300 ml.) was heated

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[11] Levi, *Gazzetta*, 1929, **59**, 548.

[12] Naylor and Hook, U.S.P., 2,723,969/1955; *Chem. Abs.*, 1956, **50**, 4548.

under reflux for 1 hr., and the solvent was then evaporated *in vacuo*. The residue was extracted with boiling ethanol (200 ml.) from which the *thiolsulphate* (11·3 g., 48%) crystallized as needles, m. p. 151° (decomp.) (Found: C, 34·2; H, 3·4; S, 22·3. $C_8H_7O_5S_2Na,\frac{1}{2}H_2O$ requires C, 34·4; H, 2·9; S, 23·0%). The *anilinium salt* crystallized from water as needles, m. p. 161° (Found: C, 49·9; H, 4·7; N, 4·3; S, 18·6. $C_{14}H_{15}NO_5S_2$ requires C, 49·3; H, 4·4; N, 4·1; S, 18·8%). Treatment of an aqueous solution of sodium phenoxycarbonylmethyl thiolsulphate with bromine water gave a precipitate of *di(phenoxycarbonylmethyl) disulphide*, m. p. 117° (from methanol) (Found: C, 57·8; H, 4·2; S, 19·1. $C_{16}H_{14}O_4S_2$ requires C, 57·5; H, 4·2; S, 19·2%).

Sodium Ethoxycarbonylmethyl Thiolsulphate.—Similar reaction of ethyl chloroacetate and sodium thiosulphate gave *sodium ethoxycarbonylmethyl thiolsulphate* (64%), as prisms, m. p. 155° (from ethanol) (Found: C, 21·4; H, 3·3; S, 28·4. $C_4H_7O_5S_2Na$ requires C, 21·6; H, 3·2; S, 28·9%).

NN'-*Dicyclohexyl(thio-oxamide).*—(i) Sodium phenoxycarbonylmethyl thiolsulphate (0·5 g.) and cyclohexylamine (5 ml.) were heated under reflux for 5 min., cooled, and dissolved in ethyl acetate (30 ml.). The solution was washed with dilute hydrochloric acid and water, dried, and evaporated. Crystallization of the residue from ethanol gave *NN'*-dicyclohexyl-(thio-oxamide) (0·36 g., 73%) as yellow plates, m. p. and mixed m. p.[1] 165°.

(ii) Similar reaction of sodium ethoxycarbonylmethyl thiolsulphate (1·0 g.) with cyclohexylamine and crystallization of the product from ethanol gave *NN'*-dicyclohexyl(thio-oxamide) (0·31 g., 26%).

NN'-*Dibenzyl(thio-oxamide).*—(i) Sodium phenoxycarbonylmethyl thiolsulphate and benzylamine were heated at 150° for 5 min., and the product was isolated in the usual way. *NN'*-Dibenzyl(thio-oxamide) (45% yield) formed yellow needles, m. p. 118—119°, from ethanol (Found: C, 67·6; H, 5·7; S, 11·4. $C_{16}H_{16}N_2OS$ requires C, 67·6; H, 5·7; S, 11·3%).

(ii) Reaction of sodium ethoxycarbonylmethyl thiolsulphate and benzylamine gave *NN'*-dibenzyl(thio-oxamide) (52% yield).

No crystalline products could be obtained by reaction of either Bunte salt with morpholine, diethylamine, or dicyclohexylamine.

NN'-*Diphenyl(thio-oxamide).*—Reaction of sodium phenoxycarbonylmethyl thiolsulphate (0·5 g.) and boiling aniline (5 ml.) for 5 min. gave a crude product from which *NN'*-diphenyl-(thio-oxamide) (0·11 g., 23%) was obtained as yellow needles, m. p. and mixed m. p.[1] 143° (from ethanol).

Thio-oxamides derived from N-*Chloroacetyl*-N'-*phenylhydrazine.*—*N*-Chloroacetyl-*N'*-phenylhydrazine [13] (30 g.) and sodium thiosulphate (1 equiv.) were heated in aqueous ethanol for 30 min. The solvent was evaporated and the residue extracted with boiling ethanol. The crude Bunte salt (17 g.) crystallized on cooling. It was very hygroscopic; the cyclohexylammonium and *S*-benzylthiouronium salts were also very soluble in water and could not be prepared in the usual way.

Reaction of the crude Bunte salt with cyclohexylamine under reflux for 10 min. gave *NN'*-dicyclohexyl(thio-oxamide), m. p. 165°, in about 10% yield.

Similar treatment of the crude Bunte salt with benzylamine gave *NN'*-dibenzyl(thio-oxamide), m. p. 118°, in low yield.

Sodium Phenacyl Thiolsulphate.—A mixture of phenacyl chloride (15·5 g.) in ethanol (50 ml.) and sodium thiosulphate pentahydrate (25 g.) in water (50 ml.) was heated to the b. p. and then evaporated to dryness under reduced pressure. The residue was extracted with boiling ethanol (150 ml.) from which the *Bunte salt* (18·0 g., 70%) crystallized as plates (Found: C, 37·7; H, 3·1; S, 25·0. $C_8H_7O_4S_2Na$ requires C, 37·8; H, 2·8; S, 25·2%). Baker and Barkenbus [14] describe the salt as a monohydrate. The infrared spectrum (KBr disc) showed strong absorption at 1673 $cm.^{-1}$ (CO group).

Oxidation of the Bunte salt with bromine water gave diphenacyl disulphide, m. p. 81° (lit.,[14] 81°). Infrared spectrum (KBr disc), 1665 $cm.^{-1}$ (CO group).

4-*Benzoyl(thioformyl)morpholine.*—A solution of sodium phenacyl thiolsulphate (1·0 g.) in morpholine (10 ml.) was heated at 100° for 15 min. 4-*Benzoyl(thioformyl)morpholine* (0·64 g., 69%), isolated in the usual way, crystallized from ethanol as yellow plates, m. p. 117° (lit.,[16]

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[13] Gattermann, Johnson, and Holze, *Ber.*, 1892, **25**, 1080.

[14] Baker and Barkenbus, *J. Amer. Chem. Soc.*, 1936, **58**, 262.

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114°) (Found: C, 61·2; H, 5·5; N, 5·4; S, 13·4. Calc. for $C_{12}H_{13}NO_2S$: C, 61·3; H, 5·6; N, 6·0; S, 13·6%). Infrared spectrum (CCl_4 solution), 1673 cm.$^{-1}$ (CO group).

Oxidation with peracetic acid (40%) at 80° for 2 min. gave benzoic acid.

4-*Acetyl(thioformyl)morpholine*.—Bromoacetone (34 g.) in ethanol (100 ml.) and sodium thiosulphate pentahydrate (62 g.) in water (100 ml.) were heated at 65° for 10 min. Morpholine (50 ml.) was added to the hot solution. After 15 min. the mixture was acidified and extracted with ethyl acetate. Evaporation of the extract gave 4-acetyl(thioformyl)morpholine (8·0 g.), yellow needles, m. p. 125—126° after crystallization from ethanol (Found: C, 48·6; H, 6·3; N, 7·7; S, 18·8. $C_7H_{11}NO_2S$ requires C, 48·5; H, 6·4; N, 8·1; S, 18·5%).

We thank Mr. J. B. Caldwell for technical assistance, and Dr. E. Spinner for determination of the infrared spectra.

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[*Received, June 8th*, 1960.]