A New Organic Reagent for Metals, Particularly Silver

BY S. E. SHEPPARD AND H. R. BRIGHAM

In the course of an investigation on the synthesis of sulfide sensitizers for photographic emulsions, a compound was isolated which derived from an interaction of glycine ethyl ester and carbon disulfide. Both aqueous and alcoholic solutions give a purple compound with even very dilute silver solutions. After various preliminary trials, the following method of preparation was adopted.

Glycine ethyl ester hydrochloride was treated with dry silver oxide in anhydrous ether.[1] The silver chloride formed was filtered off and the ethereal solution of the free ester dried over anhydrous sodium sulfate. The greater part of the ether was evaporated, the residue dissolved in absolute alcohol, and refluxed with excess of carbon disulfide. The diethyl aminoacetatedithiocarbamate was isolated, and refluxed with anhydrous alcohol and more carbon disulfide—further excess of which appeared necessary for the formation of the orange body. During this stage it was observed that hydrogen sulfide is eliminated. The crystals thus obtained appeared to be identical in properties and composition with those previously prepared by less satisfactory methods. They were recrystallized from ethylene chlorohydrin.

The melting point was 276–280° (uncorr.) and a molecular weight of approximately 200 was found by the freezing point method, using thymol as solvent.

It was very soluble in aniline, phenol, thymol and hot ethylene chlorohydrin; soluble in hot acetophenone; slightly soluble in acetone, acetic acid and in hot benzene, butyl alcohol, chloroform, ethyl acetate and heptane; insoluble in carbon tetrachloride, ligroin and water. Its red solutions in acetophenone, benzene, butyl alcohol and chloroform would not recrystallize. Ethylene chlorohydrin was most useful for recrystallization.

Analyses and Derivatives

Ultimate analysis[2] gave the following results.

TABLE I

		C	H	N	O	S
Calcd. for	$C_7H_{10}N_2O_3S$	41.6	4.95	13.86	23.75	15.85
	$C_7H_8N_2O_3S$	42.00	4.00	14.00	24.00	16.00
Found		41.92	4.02	13.6	24.7	15.9

The substance contained a saponifiable ethyl ester group, which was determined by saponifying with alkali, and back titrating the excess, using the substance itself as an indicator, since the sodium and potassium salts are colored, while in acid it is nearly colorless.

Beside showing (by the saponification) the presence of one C_2H_5OCO group in the molecule, it gives a positive

reaction with chloropicrin for potential mercaptans, indicating the presence of a mobile $\overset{H}{\underset{}{>}}C{=}S \rightleftharpoons {>}CSH$ group.[3] Further, it forms definite lead and silver compounds.

The **lead salt** was prepared by treating a solution of the orange compound with a solution of lead acetate and precipitated as a steel blue microcrystalline compound. It was washed well with water and alcohol, but could not be recrystallized because of its very low solubility. It is decomposed by dilute mineral acid. On heating the dry compound for some time at 110° it decomposes, giving lead sulfide.

Anal. Calcd. for $C_7H_8N_2O_3SPb$: C, 20.58; H, 1.95; N, 6.31; O, 14.28; S, 6.98; Pb, 49.9. Found: C, 20.62; H, 1.96; N, 6.87; O, 11.80; S, 7.86; Pb, 50.80.

The **silver salt** was prepared in a manner similar to the lead salt, to which it has similar properties, but differs in color, this being a deep purple.

Anal. Calcd. for $C_7H_8N_2O_3SAg$: Ag, 34.95. Calcd. for $C_7H_8N_2O_3SAg_2$: Ag, 51.8. Found: Ag, 47.5.

Reactions with Metals and Sensitivity

The orange compound gives precipitates of different colors with various metals in neutral solutions, but in acid solution only silver ions react to give a colored insoluble salt. The solutions of the metals were of approximately 0.01 g. of the metal ion in 10 cc. of solutions; they were tested with 0.5 cc. of the reagent at 0.03% solution in acetone.

The metals tested in a neutral solution gave the following colors: silver, purple; cadmium and ammonium, red; copper, red-blue; iron, yellow; lead, blue; zinc, pink; and manganese and tin a white precipitate. On the other hand, in acid solution, silver gave a purple solution, while all the other metals gave a yellow solution with the exception of manganese and tin which gave white precipitates.

To determine the sensitivity of the new reagent for silver ion, in comparison with Feigl's reagent, solutions of silver ion of various concentrations were made up and tested by the procedure given by Kolthoff.[4] To 10 cc. of the silver solution were added 0.5 cc. of 4 N nitric acid, followed by 0.3 cc. of a 0.03% solution in acetone of the reagent.

TABLE II

G. of silver per cc.	Color of solution, Feigl's reagent	Color of solution Orange Compound
1×10^{-4}	Red	Red (bluish)
1×10^{-5}	Red	Red
1×10^{-6}	Pink-orange	Orange
5×10^{-7}	Orange	Yellow-orange
2×10^{-7}	Slight orange	Yellow
1×10^{-7}	Very slight tint	Yellow
Blank	Colorless	Yellow

(1) T. Curtius and F. Goebel, *J. prakt. Chem.*, **37**, 164 (1888).

(2) Our thanks are due to Dr. L. Hallett, Organic Research Laboratory, for these analyses.

(3) P. C. Ray and R. Das, *J. Chem. Soc.*, **121**, 323 (1922).

(4) I. M. Kolthoff, THIS JOURNAL, **52**, 2222 (1930).

The appearance for various silver concentrations is indicated in Table II.

Under these conditions, Feigl's reagent allows 0.2 mg. silver per liter, or 1 part in 5,000,000 to be detected, and the new reagent only 1 part per 1,000,000. This is because of the pronounced yellow color of the blank. With a lower concentration of nitric acid, a higher sensitivity was obtained. To 10 cc. of the silver solution one drop of 4 N nitric acid is added, followed by 2 drops of a 0.03% solution of the reagent in acetone. The results are tabulated in Table III.

TABLE III

G. of silver per cc.	Color of solution
1×10^{-4}	Pink
1×10^{-5}	Pink
1×10^{-6}	Pink
5×10^{-7}	Pink
3×10^{-7}	Pink
2×10^{-7}	Pink
1×10^{-7}	Yellow
Blank	Pale yellow

By this procedure the reagent detects silver at 1 part in 5,000,000.

Since Feigl's reagent, prepared by the condensation of p-dimethylaminobenzaldehyde with rhodanine gives a much greater color intensity with silver ion than rhodanine, it appears feasible that the same or a similar condensation with the new reagent should also greatly increase the sensitivity by the introduction of further chromophore groupings but attempts to do this have not been successful so far, apparently by reason of the difficulty of finding a common inert solvent for the two substances.

The Structure of the Compound

In the study of the reaction, it was observed that hydrogen sulfide is released in the later stage. A reaction which includes the splitting off of hydrogen sulfide and of a molecule of ethyl alcohol from diethylaminoacetatedithiocarbamate (I) is shown in A.
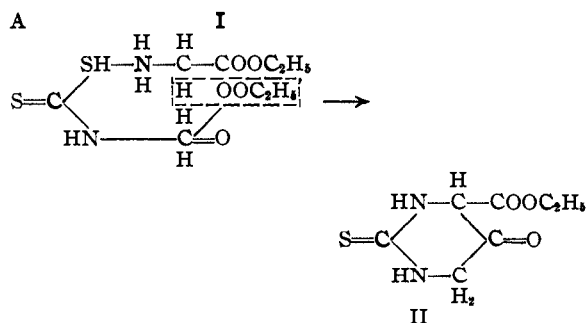

The heterocyclic ring compound thus produced has (i) the empirical formula $C_7H_{10}N_2O_3S$; (ii) a $\rangle C{=}S$ group readily tautomerized to $\rangle C{-}SH$; (iii) two replaceable hydrogens, allowing formation of Pb and Ag salts as found; (iv) a saponi-

fiable ethyl ester group. This compound would be   2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimi-dine, (II). It should be possible to confirm this by the following independent synthesis
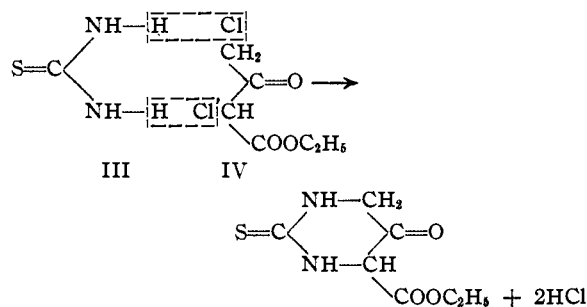
i. e., the condensation of thiourea (III) with ethyl α,γ-dichloroacetoacetate (IV).

A pilot condensation of the foregoing type was made by heating together on a steam-bath for an hour α,γ-dichloroacetone and thiourea
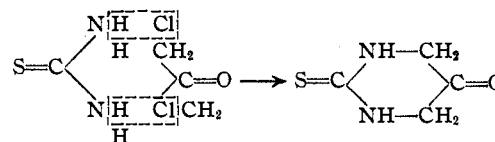
Hydrochloric acid was eliminated, and after evaporation of the reaction mixture in a vacuum desiccator white crystals separated. These were recrystallized from alcohol. They melted with decomposition and evolution of gas at 241°.

Anal.   Calcd. for $C_4H_6N_2OS$: S, 24.61; N, 21.53. Found: S, 24.3; N, 21.4.

This substance gave a white precipitate with silver ions, which decomposed to silver sulfide on heating. Although this synthesis appeared successful, attempts to carry through the same type of reaction, using ethyl α,γ-dichloroacetoacetate in place of α,γ-dichloroacetone failed. There was elimination of hydrochloric acid, but a reddish-brown viscous oil was obtained which could not be crystallized.

The highly colored and very slightly soluble silver compound resembles that produced with Feigl's reagent for silver ion.[5] This reagent is p-dimethylaminobenzalrhodanine. It seemed possible that a rhodanine or analog might have been produced by a condensation reaction. For example, rhodanine (V) is formed by the condensation of ammonium dithiocarbamate with ethyl chloroacetate[6] as follows
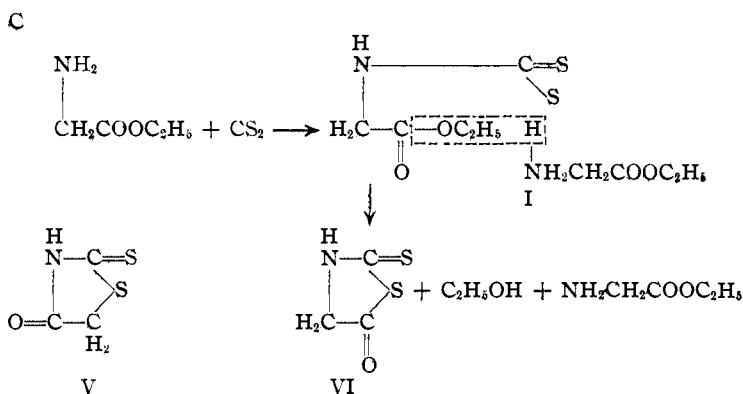
(5) K. Feigl, Z. anal. Chem., **74**, 380 (1928).

(6) A. Miolati, Ann., **262**, 85 (1891).

B

V
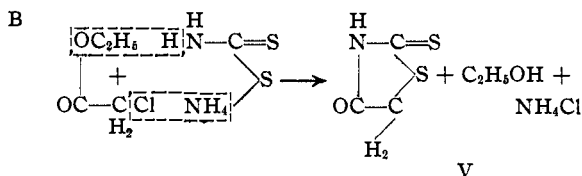
Again, Holmberg[7] and Buck and Leonard[8] have shown that ammonium salts of dithiocarbamate react with potassium chloracetate in an analogous manner.
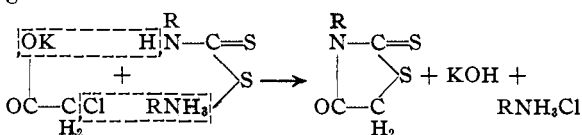

It appeared possible therefore in the present case that a reaction might have occurred as represented under C.

C

The series of reactions in C are nearly parallel to those under B, the molecule of ammonia being replaced by a second molecule of the glycine ethyl ester itself, forming *diethyl aminoacetatedithiocarbamate* (I) (which, as already mentioned, was isolated as an intermediate in the production of the orange compound). This could then split off alcohol and glycine ethyl ester to form a *pseudo*-rhodanine (or *pseudo*-rhodanic acid) (VI). It is designated *pseudo*-rhodanine to distinguish it from the true rhodanine (V), which has the oxygen on the 4-carbon atom, whereas in (VI) it is in the 5-position. However, the empirical analyses point to a formula $C_7H_{10}N_2O_3S$, a considerably larger molecule than that of the pseudo-rhodanine. Furthermore, there is only *one* sulfur found in the molecule, and this cannot be in the ring because of its positive reaction for potential mercaptans.

Another course of the original reaction is feasible, leading to a product of the same empirical

composition and molecular weight. The scheme for this reaction is as follows

I   VII
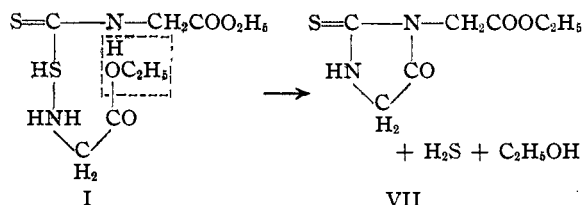
The product formed would be *2-thiohydantoin-3-ethylacetate* (VII), having the required empirical composition and molecular weight. Further, the reaction schematized proceeds with elimination of hydrogen sulfide. On the other hand, the structure does not allow for two replaceable hydrogens, corresponding to the silver and lead salts previously described. To clear up the matter, the thiohydantoin was synthesized by an independent method based on that of Johnson and Renfrew,[9] which gave ultimately *2-thiohydantoin-3-acetic acid*. This latter was esterified with ethyl alcohol saturated with hydrogen chloride gas. The compound produced formed yellow crystals, melting 95.5–96.6°.

Anal. Calcd. for $C_7H_{10}N_2O_3S$: N, 13.86. Found: N, 13.88.

The compound is soluble in water, and gives an immediate deposit of silver sulfide with silver ions. It appears evident that the thiohydantoin does not correspond to the orange compound, and therefore this alternative reaction and this constitution are eliminated. This leaves the thiopyrimidine structure as the most probable.

Summary

1. A compound prepared by refluxing *diethyl aminoacetatedithiocarbamate* with anhydrous ethyl alcohol and carbon disulfide was found to give strongly colored compounds with a large number of metals at very low concentration. In particular, it shows a high sensitivity to silver in solutions sufficiently acid to inhibit its reaction with other metal ions.

2. From empirical and group analyses it is concluded that the new reagent is *2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine.*

3. The sensitivity to silver ion has been determined. It can be made about equal to that of

(7) B. Holmberg, *J. prakt. Chem.*, [1] 79, 253 (1909).

(8) J. S. Buck and C. S. Leonard, This Journal, 53, 2688 (1931).

(9) T. B. Johnson and A. G. Renfrew, *ibid.*, 47, 240 (1925).

Feigl's reagent, viz., detection of 1 part in 5,000,-000. It is suggested that this might be considerably increased if the substance can be condensed with substituted benzaldehydes.

4. Under conditions of highest sensitivity (weak acidity), the reagent is more selective for silver than Feigl's reagent.

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The Dipole Moment of Ammonia in Solution

BY W. D. KUMLER

The ammonia molecule is one of the rare cases in which one of the vibrations of the molecule causes an inversion of the dipole moment. Evidence for this vibration was obtained from the spectrum.[1] The period of the vibration is about 10^{-10} seconds and the movement responsible for the effect is a shifting of the nitrogen atom with respect to the plane of the hydrogen atoms.[1,2]

1 $N\!\!\!<^{H}_{H}\!\!-H\!\!\rightarrow\!N$ 2. When the nitrogen is in position 2 the molecule will have a moment equal to but just opposite in direction to the moment when the nitrogen is in position 1. This inversion of the moment will have an effect on the dipole moment as measured in solution depending on whether the inversion time is greater or less than the relaxation time τ of the orientation in the electric field. The polarization due to dipole orientation reaches a maximum τ seconds later than the field so if the time of inversion is less than τ, the molecule will invert before the maximum polarization is obtained and the field will tend to give the inverted molecule angular momentum opposite in direction to that given it originally. Before the new orientation can reach a maximum the inversion again takes place, etc. As the time of inversion decreases with respect to τ, the limiting condition is one in which the molecule virtually stands still, in which case it would give no evidence of possessing a dipole moment.

Some of the earlier work seemed to indicate a time of relaxation in the usual organic solvents of about 10^{-7} second,[3] in which case ammonia should have a very small or zero moment in solution. More recently Debye[4] has determined the time of relaxation in organic solvents by means of high frequency energy absorption and finds it to be of

the order of 10^{-12} second, in which case ammonia would be expected to have a dipole moment in solution differing from that in the gas by only a small amount, due to the solvent effect.[5]

I have measured the dipole moment of ammonia in benzene and in n-heptane and find it to be 1.38×10^{-18} e. s. u. in benzene and 1.43×10^{-18} e. s. u. in n-heptane. The average value of five determinations taken from the literature of the dipole moment of ammonia in the gaseous state is 1.47×10^{-18} e. s. u.[6] The moment in solution is less than in the gas but the discrepancy is not of a greater magnitude than can be accounted for by the solvent effect. The value of the moment in benzene and n-heptane is evidence that the time of relaxation in these solvents is less than the time of inversion of the molecule.

Results

In Table I the symbols are: ω the weight fraction of the solute, d the density of the solution, ϵ the dielectric constant of the solution, P_2 the polarization of the solute, P_{E_2} the electronic polarization of the solute, μ the dipole moment.

TABLE I
AMMONIA IN BENZENE

ω	d	ϵ	P_2
0.00	0.87212	2.26700	
.0008799	.87154	2.27685	46.19
.0015437	.87116	2.28473	46.77
.0024244	.87068	2.29459	46.17
.0039526	.87003	2.31281	46.29

AMMONIA IN n-HEPTANE

ω	d	ϵ	P_2
0.00	0.679306	1.90936	
.0003859	.679264	1.91281	50.67
.0012537	.678932	1.92020	50.81
.0020071	.678536	1.92468	46.44

	P_{E_2}	$\mu \times 10^{18}$
Ammonia in benzene	6.5	1.38
Ammonia in n-heptane	6.7	1.43

(1) Dennison and Hardy, Phys. Rev., **39**, 938 (1932).
(2) Rodebush, Trans. Faraday Soc., **30**, 783 (1934).
(3) Ebert, Leipziger Vorträge, Leipzig, 1929, p. 55.
(4) Debye, Trans. Faraday Soc., **30**, 679 (1934).

(5) Müller, ibid., **30**, 729 (1934).
(6) Table of Dipole Moments, ibid., **30**, XI (1934).