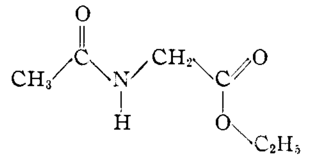
sult may be considered to indicate in the first place that the NH bond and the peptide CO bond are almost parallel to each other and, accordingly, the peptide bond has a planar *trans* configuration as in the case of N-methylacetamide[3] and acetylamino acid N-methylamides.[2] It may show in the second place that the angle between the peptide CO bond and the ester CO bond is not much different from the right angle and the molecular configuration of AGEt in the crystalline state cannot be the extended form as in the case of ALNA. A probable form would be



A completely folded form just like that shown in Fig. 1 may also be possible. It is easily seen that even the partially folded form shown above would not be as readily associated through intermolecular hydrogen bond as the extended form, while the completely folded form would have the least tendency to be associated. Thus we can see the reason why the association of this substance is less pronounced as compared with N-methylacetamide, for which no hindrance of the intermolecular hydrogen bond can occur.

The experimental results obtained in the present work provide us with further information regarding the structure of some simple molecules which would permit the reliable prediction of the structure of the polypeptide chain.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Photolysis of Some Mercury Dimercaptides

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When mercury dibenzyl mercaptide is photolyzed in benzene solution, mercury, mercuric sulfide, benzyl disulfide, dibenzylbenzal mercaptal and benzyl sulfide are formed. Mercury diphenyl mercaptide forms free mercury but no mercuric sulfide under the same conditions. Six mercury dimercaptides were found to vary markedly in their susceptibilities to photolysis in the solid state the order of increasing stability being benzyl, *n*-propyl, isopropyl, cyclopentyl, *t*-butyl and phenyl.

In the course of preparing derivatives of thiols it was noticed that mercury dimercaptides turned dark on standing, a fact previously recorded by Marcker.[2] A black precipitate insoluble in benzene and a benzene-soluble mixture formed on the photolysis of a benzene solution of mercury dibenzyl mercaptide under nitrogen. Analysis of the insoluble solids indicated 96.3% mercury and 3.5% sulfur which corresponds to 77% of total mercury in the elemental state and 23% as mercuric sulfide. The benzene-soluble portion consisted of 78% benzyl disulfide, 13% dibenzylbenzal mercaptal and a small amount of benzyl sulfide.

A dimercaptide molecule may be considered as decomposing in some manner *via* either (1) or (2). If 77% of the mercaptide molecules decompose

$$(C_6H_5CH_2S)_2Hg \longrightarrow 2[C_6H_5CH_2S\cdot] + Hg^0 \qquad (1)$$

$$(C_6H_5CH_2S)_2Hg \longrightarrow [C_6H_5CH_2S\cdot] + [C_6H_5CH_2\cdot] + HgS \qquad (2)$$

according to (1) and 23% by (2) then dimerization of the organic units in (1) would theoretically give rise to 79% benzyl disulfide in the organic products.

Mercury diphenyl mercaptide irradiated under the same conditions produced only free mercury and no mercuric sulfide. Lecher[3] found this also to be the case on pyrolysis of this compound. Mercury from the photolysis of mercury dicyclopentyl mercaptide appeared 72% in the elemental state and 28% as mercuric sulfide.

The difference between the photolyses of benzyl and phenyl analogs may be related to the relative stabilities of the corresponding thio-free radicals. The thiophenyl radical would be expected to receive greater stabilization due to resonance structures not available to the thiobenzyl radical. Being relatively more stable only thiophenyl radicals and free mercury are formed from the diphenyl mercaptide while an alternative course of decomposition is also followed by the dibenzyl compound resulting in formation of mercuric sulfide. Phenyl disulfide dissociates to a greater degree than benzyl disulfide as indicated by the fact that when used as photosensitizers in the photopolymerization of styrene 93% conversion is effected by the former compared to 20% by benzyl disulfide under identical conditions.[4]

Six mercury dimercaptides were prepared and irradiated in the solid state by a cold germicidal lamp producing essentially 2537 Å. radiation. These compounds could be arranged in a series according to susceptibility to photolysis judging this by the extent of discolorations under as nearly identical radiation conditions as could be obtained. The benzyl member was the most susceptible turning a jet black color while the phenyl member remained practically unaffected. The series in apparent decreasing susceptibility under these conditions was benzyl > *n*-propyl > isopropyl $\cong$ cyclopentyl > *t*-butyl > phenyl. These differences were not apparent when photolyses were carried out in benzene solution.

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(1) Monsanto Chemical Co., Dayton 7, Ohio.

(2) C. Marcker, *Ann.*, **136**, 81 (1865).

(3) H. Lecher, *Ber.*, **48**, 1425 (1915).

(4) L. M. Richards, U. S. Patent 2,460,105 (1949).

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Experimental

Mercury Dibenzyl Mercaptide.—A suspension of 21.6 g. (0.1 mole) of mercuric oxide in 50 cc. of methanol and 30 cc. of chloroform was added in portions to a solution of 24.8 g. (0.2 mole) of benzyl mercaptan (EK 1509) in 20 cc. of chloroform using magnetic stirring. After the resulting mixture had been stirred one-half hour a filter aid (celite) was added and the hot solution filtered. Filtering was repeated as often as necessary to obtain a clear solution. The solvent was removed and the residue crystallized from benzene to yield 32 g. (75%) of silky strands, m.p. 120–121°.

Anal. Calcd. for $C_{14}H_{17}S_2Hg$: C, 37.62; H, 3.16. Found: C, 37.57; H, 3.08.

Conditions for Photolysis.—Five grams of the mercaptide was dissolved in 200 cc. of thiophene-free benzene and irradiated under a nitrogen atmosphere in a Vycor flask by a Hanovia 95-watt type SH A-C mercury arc lamp. Magnetic stirring was employed; heat from the lamp kept the temperature between 60–70°. An opalescence quickly formed becoming an olive turbidity, then a jet black sediment. About every three hours the reaction mixture was allowed to settle, the clear solution decanted off and irradiated again, the solid product being collected. Vessel walls were cleaned about every six hours with aqua regia, the washings being kept for mercury analysis. Generally 15 hours of radiation were sufficient to effect complete photolysis. This was done until 20.05 g. of mercaptide had been photolyzed.

Analysis of Products.—The black benzene-insoluble product which had been collected was placed in a filtering crucible and thoroughly washed with benzene, carbon disulfide and acetone, dried, and weighed (8.48 g.). Evaporation of these washings revealed no appreciable material. The solid was analyzed for mercury gravimetrically as mercuric sulfide and for sulfur by sodium peroxide oxidation to sulfate and precipitation as barium sulfate[5]; 96.3% mercury and 3.5% sulfur were found. Mercury in this material plus that found in the aqua regia washings (0.46 g.) amounted to 96% of the mercury in the original mercaptide. These results were repeated in a second experiment.

Soluble organic products were in the benzene solution which was filtered and distilled from a steam-bath under reduced pressure. A golden yellow residue remained which was taken up in ether and cooled. Any undecomposed starting material crystallized at this point in the form of silky strands. A test for mercaptan consisting of a few drops of aqueous lead acetate, sodium hydroxide solution and a cc. of the ether solution was negative. A yellow precipitate would have denoted presence of mercaptan.[6] The ether was removed leaving 10.0 g. of tan solid material (I), m.p. 58–68°. Benzyl disulfide was qualitatively separated by fractional crystallization from ethanol and identified by m.p. (71°) and mixed m.p. with authentic material (EK 1602). Weighed amounts of I were reduced in a solution of 25 cc. of 95% ethanol and 1 cc. of concd. sulfuric acid with amalgamated zinc by a method adapted from that of Kolthoff.[7] One hour at 50–60° with occasional shaking was found sufficient for reduction. The mercaptan produced was titrated with standard iodine solution. Samples of known benzyl disulfide ranging from 0.2 to 0.6 g. with or without benzyl sulfide added gave results averaging 97%. I was determined as being 78% disulfide in this manner. This value was checked by a second independent experiment.

Another portion of I was reduced as above, most of the ethanol removed by evaporation, and the residue taken up in petroleum hexane. This was extracted with 1 M sodium hydroxide and evaporated. The residue was placed in a cold room three days whereupon partial crystallization occurred. This mushy material was spread on a piece of porous plate. After a day 0.08 g. of glistening white solid remained which melted at 61° and proved to be dibenzylbenzal mercaptal by mixed m.p. with an authentic sample.[8] When oxidized with 30% hydrogen peroxide in glacial acetic acid a compound (the disulfone) melting at 210–212° with decomposition formed. The mixed m.p. with the oxidation product from the authentic material was identical. The porous plate was ground up in a mortar and extracted with methanol. Excess 5% solution of mercuric chloride in ethanol was added and an amorphous white solid weighing 0.11 g. filtered off. Dibenzylbenzal mercaptal cleaves under these conditions to form chloromercury benzyl monomercaptide and benzaldehyde.[9] Based on the mercaptal isolated as such and the chloromercury monomercaptide resulting from cleavage, 13% of I was determined as being dibenzylbenzal mercaptal. Upon concentration of the alcoholic filtrate and cooling 0.09 g. of well formed prisms appeared which melted from 133–136°. Mixed m.p. with the mercuric chloride complex of known benzyl sulfide (EK 1510) was the same.

Another portion of I was reduced, extracted of benzyl mercaptan and treated with alcoholic mercuric chloride as above. The mixture was evaporated by air stream and extracted with petroleum hexane which was then filtered and evaporated. A very small amount of sirupy material remained possessing a strong odor of dibenzyl but no positive chemical identification could be made on several attempts.

Comparative Photolyses in the Solid State.—The procedure described for the benzyl analog was used to prepare all the dimercaptides except that petroleum hexane was used to recrystallize the cyclopentyl, *n*-propyl, and isopropyl members of the series. All m.p.'s agreed with values in the literature.[10] Mercury dicyclopentyl mercaptide[11] melts at 43°. Samples were irradiated beneath a 15-watt General Electric germicidal lamp. Differences became fully apparent after 12 hours of radiation at a distance of three to four inches.

Comparison of the Photolysis of Mercury Dibenzyl Mercaptide and the Phenyl Analog in Benzene Solution.—Forty-five cc. quantities of 0.01 M thiophene-free benzene solutions of the two dimercaptides were irradiated in Pyrex test-tubes for 45 minutes with a Hanovia type SH mercury arc lamp, magnetic stirring being employed. The sediment which formed was filtered off, washed and weighed. An average of 0.057 ± 0.007 g. of material was obtained over the course of nine trials for the benzyl compound to be compared with 0.063 ± 0.004 g. for eight trials using the phenyl analog. On filtering off the solid product from the phenyl compound it formed the silvery globules typical of free mercury.

EVANSTON, ILL.

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