No effort was made to identify specifically the water present, but the products were interconvertible. A mixture of the two had approximately the average m. p. (165°).

A sample of the isomeric 1-anilide made for comparison from the phenylimide, m. p. 181°; a mixture with the 2-anilide (m. p. 154°) m. p. 153°. The melting points are too far apart for a definite depression to be expected.

3-Nitrophthalic Acid-1-anilide-2-amide.—Four grams of the phenylimide was dissolved in 20 cc. of absolute alcohol containing 3 cc. of concentrated ammonium hydroxide, the mixture warmed for half an hour at 50°, and then diluted and acidified. The product, from acetone, m. p. 200–204° (depending on the rate of heating) with effervescence.

Anal. (Kjeldahl) Calcd. for $C_{14}H_{11}O_4N_3$: N, 14.74. Found: N, 14.79.

3-Nitrophthalic Acid-1-amide-2-anilide.—The imide (IV) remained unchanged after warming for an hour at 100° with 1 mole of aniline in 20 cc. of benzene. After two hours with 4 moles of aniline without solvent, reaction had taken place. Crystallized from acetone or from alcohol, the product showed m. p. 228–230°.

Anal. (Kjeldahl) Calcd. for $C_{14}H_{11}O_4N_3$: N, 14.74. Found: N, 14.58.

Summary

1. In the case of unsymmetrical acid anhydrides and acid imides, the assumption that the ring is opened in each case at the bond connected to the *same* carbonyl group, requires that when (as is usually the case) one of the two possible amides is chiefly formed from the anhydride and ammonium hydroxide, *the other* amide should result from the alkaline hydrolysis of the imide.

2. Over the limited range studied, this principle is confirmed.

BELTSVILLE, MD. RECEIVED FEBRUARY 6, 1935

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies in Thiophenol Chemistry. II. A Reaction between Aromatic Mercaptals and Formaldehyde

BY WENDELL H. TAYLOR

Since their discovery fifty years ago by E. Baumann, the thioacetals[1] have been classed among the more inert organic compounds. Although recent work has greatly enlarged our knowledge of those thioacetals derived from mercaptans and ketones (the so-called mercaptoles) little has been done with the mercaptals, or aldehyde derivatives, which appear to be much less reactive.

In the continuation of a study of the general problem of thiophenol–formaldehyde condensations[2] it has been found that a reaction takes place between aromatic mercaptals and formaldehyde in acid media, yielding crystalline products. These are of particular interest in view of the reactivity and tendency to rearrangement exhibited by the analogous acetals, which play an important part in many mechanisms suggested[3] for the formation of phenol-formaldehyde resins.

Slow Reaction of Mercaptals with Formaldehyde.—If formaldehyde diphenylmercaptal, $CH_2(SC_6H_5)_2$, is prepared by direct condensation as described in the Experimental Part of this paper, it separates from solution as a colorless oil which may be crystallized, and melts after purification at 36°. If, however, the oily product is not removed from the flask but is allowed to remain in contact with acetic acid, hydrogen chloride and excess formaldehyde over a period of several months it is slowly converted into a solid, waxy mass having properties quite unlike those of the mercaptal. This change will not take place unless there is present more than enough formaldehyde to combine completely with the thiophenol employed in the initial condensation. By raising the temperature to the boiling point of acetic acid the reaction may be brought about in a few hours, and since the products obtained are the same they are described together in the next section.

Rapid Reaction of Mercaptals with Formaldehyde in Hot Acid Solution.—When various pure, crystalline mercaptals are dissolved in glacial acetic acid, treated with a moderate excess of formaldehyde, the solution then saturated with hydrogen chloride and refluxed for several hours, there separate from solution crystalline products of much higher melting point than the original

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(1) The literature concerning these compounds is summarized by A. Schönberg in Vol. 19 of Ahrens' *Sammlung* (1933); additional references are given by Malisoff, Marks and Hess in *Chem. Rev.*, **7**, 508 (1930).

(2) Dougherty and Taylor, THIS JOURNAL, **55**, 4588 (1933).

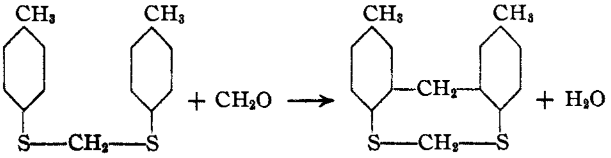
(3) Scheiber and Sändig, "Die künstlichen Harze," Stuttgart, 1929, p. 133.

mercaptal, and of much greater insolubility. These products do not form in the absence of any one of the four reactants named above, but under the conditions later described in detail from one-third to two-thirds of the weight of the original mercaptal can be isolated in the form of the new product.

The substances produced fall sharply into two groups, depending upon the nature of the parent mercaptal. Mercaptals formed from various aldehydes and unsubstituted thiophenol yield colorless products, microcrystalline after purification, very sparingly soluble in the common solvents and all exhibiting double melting points on rapid heating. Analysis shows a composition not very different from that of formaldehyde diphenylmercaptal, but varying slightly from sample to sample because of the difficulty of recrystallization, while molecular weight determinations give values ranging from one to four times the molecular weight of $CH_2(SC_6H_5)_2$. Most important is the fact that the products are free of elements other than carbon, hydrogen and sulfur, irrespective of the nature of the aldehyde residue in the parent mercaptal (*e. g.*, *m*-nitrobenzaldehyde) and are practically identical.

In the hope that mercaptals formed from substituted thiophenols would yield more definitely characterized products, *p*-thiocresol and *p*-nitrothiophenol were condensed with various aldehydes and the mercaptals thus obtained subjected to the treatment already described. Products formed from these mercaptals were fortunately well-crystallized, readily soluble and showed no tendency to further change. These substances show a single definite melting point in each case and apparently contain phenyl groups substituted as in the original thiophenol, but the nature of the aldehyde which was condensed with the thiophenol does not affect the new product. Analyses and molecular weight determinations indicate a composition corresponding to the addition of one $—CH_2—$ group to a substituted formaldehyde diphenylmercaptal $CH_2(SC_6H_4—R)_2$.

Suggested Explanation of the Reaction.— The absence from all final products of any substituent originally attached to the aldehyde group of the parent mercaptal strongly suggests that the primary change is, in effect, a replacement of the original aldehyde by formaldehyde with the resulting formation in all cases of a formaldehyde diphenylmercaptal, which may or may not be substituted in the benzene rings. This replacement is presumably facilitated by the hydrolyzing action of the acetic acid used as solvent, and the excess of formaldehyde present. The next step can be established with certainty only by a separate synthesis, which has not yet been achieved, but at least in the case of the products obtained from mercaptals of *p*-thiocresol analytical evidence strongly supports the formation of a methylene bridge between the phenyl groups of the formaldehyde mercaptal, yielding a ring of two sulfur atoms and six carbon atoms.



This condensation may take place directly, or, by analogy with the well-known rearrangements of acetals and of alkyl phenyl ethers, through the intermediate rearrangement of the mercaptal to a di-*o*-mercaptodiphenylmethane, which might then condense with the second molecule of formaldehyde. On the present evidence, the size of the ring formed can be only conjectural. Large rings containing carbon and sulfur have been well known since the work of Autenrieth[4] on the cyclomercaptals, and these may possibly be present in the products of high insolubility and double melting point obtained from mercaptals where the para-position on the benzene rings is not blocked. Smaller rings containing two sulfur atoms are not less common, though varying in the probability of their formation, as the recent work of Reid[5] has demonstrated.

Further data concerning the preparation, properties and analyses of these new products will be found in the Experimental Part of this paper. In the course of the work occasion was had to prepare several mercaptals not previously reported in the literature. Data concerning these are given. For helpful suggestions concerning this problem the author wishes to thank Professor Gregg Dougherty. The work is being continued.

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(4) Autenrieth, *et al.*, *Ber.*, **42**, 4346, 4357 (1909), and earlier papers.

(5) Tucker and Reid, THIS JOURNAL, **55**, 775 (1933); Meadow and Reid, *ibid.*, **56**, 2177 (1934).

Experimental Part

Slow Reaction between Mercaptals and Formaldehyde.—Of a large number of experiments of this type, two may be described.

(A) **Formaldehyde Diphenylmercaptal.**—Ten cubic centimeters of thiophenol, 12 cc. (a three-fold excess) of 40% aqueous formaldehyde and 20 cc. of glacial acetic acid were mixed in a 150 cc. glass-stoppered flask, giving a clear solution. In a similar flask were mixed 10 cc. of thiophenol (10.87 g.), 4 cc. of formalin (1.6 g. of formaldehyde) and 20 cc. of glacial acetic acid. Dry hydrogen chloride was then run rapidly into both solutions, with shaking, until saturation, no cooling being attempted. After about five minutes a heavy layer of formaldehyde diphenylmercaptal separated as an oil in each flask, and after cooling both were closed and the stoppers wired down. The flasks were then set aside at room temperature and observed from time to time, being shaken very occasionally. At the end of seventeen months there was no change whatsoever in the appearance of the flask containing thiophenol and formaldehyde in the exact proportions for mercaptal formation, but the mercaptal layer in the other flask (containing excess formaldehyde) had by this time been changed into a colorless, waxy mass. The beginning of this change was apparent after five months, and progressed gradually thereafter, becoming complete in about twelve months.

To the clear contents of the second flask was then added about 2 g. of formaldehyde in the form of dichlorodimethyl ether[6] and the resulting clear solution held for observation. After three weeks it had become turbid, and after five months the mercaptal layer had been converted into a soft, waxy mass, exactly similar to that in the companion experiment.

Products from both flasks were but slightly soluble in cold organic solvents, but moderately so in hot benzene, acetic acid, pyridine, thiophene or dioxane. From the last solvent were obtained small prisms, visible under a magnification of 21 diameters. These melted at 140–145° (plunging method) but when held in a bath at 150° or above the sample re-solidified, melting again at 245–250°. Molecular weight determinations in boiling benzene, dioxane or pyridine gave an average of 244; other samples which had formed over longer periods of time showed molecular weights of 542 and even 900 in boiling thiophene. Eight micro-combustions on various samples indicated C, 65.43%; H, 5.08% (average) for samples of high molecular weight, and C, 61.9%; H, 5.1% (average), for those of lower molecular weight. These varying values reflect the difficulty of purifying the insoluble materials. The parent substance, $CH_2(SC_6H_5)_2$, has a molecular weight of 232, and contains C, 67.17%; H, 5.20%; S, 27.63%.

(B) **Formaldehyde-di-*p*-tolylmercaptal.**—In an experiment similar to that in (A), using 3 g. of *p*-thiocresol, 3 cc. of formalin and 10 cc. of acetic acid saturated with hydrogen chloride, there was obtained after six months of standing a crystalline solid product which after washing with ether and recrystallization from ethyl alcohol formed lustrous scales, melting at 186–187°. This material did not show a second melting point; molecular weight in boiling benzene, 284; analysis showed C, 70.62%; H, 6.18%. Formaldehyde-di-*p*-tolylmercaptal is an oil having a molecular weight of 260 and containing C, 69.23%; H, 6.15%; S, 24.62%, while the linking of the two phenyl groups by a methylene bridge would change the composition to C, 70.58%; H, 5.9% and the molecular weight to 272.

(C) **Benzophenone Diphenylmercaptole.**—Under the conditions of the above experiments no change could be detected in benzophenone diphenylmercaptole after six months.

Reaction between Mercaptals and Formaldehyde in Boiling Acetic Acid

(A) **Preparation of Pure Mercaptals.**—These were made in every case by direct condensation of mercaptan and aldehyde in acetic acid, using hydrogen chloride as condensing agent and a slight excess over the theoretical quantity of aldehyde to ensure complete removal of the easily oxidizable mercaptan. Only in the case of the formaldehyde mercaptals did the product separate rapidly; in general the reaction mixture was allowed to stand overnight in the ice-box. Recrystallization of the resulting oily product (which usually solidified on washing) was best effected using 95% ethyl alcohol. The yields are good. Table I gives the melting points and other data for five mercaptals not hitherto prepared,[7] which were of use in this study. Several others, already reported in the literature, were investigated; reference to these is made in the next section.

TABLE I

MERCAPTALS NOT PREVIOUSLY REPORTED

Formula ($R = —C_6H_4CH(SC_6H_4—)_2$)	Appearance[a] (C = colorless)	M. p., °C. (corr.)	Calcd., % C	Calcd., % H	Found, % C	Found, % H
m-$NO_2—RH_2$	C. leaflets[b]	65.5	Not analyzed			
m-$NO_2—R(CH_3)_2$ (*p*)	C. prisms[c]	85.5	66.14	4.98	66.01	5.14
p-$CH_3—R(CH_3)_2$ (*p*)	C. needles	72	75.40	6.28	74.80	6.31
o-$NO_2—RH_2$	Cream-yellow prisms[b]	101	64.58	4.25	64.48	4.36
$C_6H_3(OH)(Br)CH{=}(SC_6H_4\text{-}p\text{-}CH_3)_2$[d]	C. silky needles	97	58.46	4.40	58.44	4.66

[a] After recrystallization from EtOH. [b] Slowly turns yellow in daylight. [c] Does not turn yellow. [d] The di-*p*-tolylmercaptal of 2-bromo-5-hydroxybenzaldehyde.

(B) **The Condensation Reaction.**—Two grams of the recrystallized mercaptal was dissolved in 30 cc. of glacial

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(6) This is readily hydrolyzed, and avoids the addition of further aqueous formaldehyde, which might have brought about immediate precipitation.

(7) The di-*p*-tolylmercaptals of *o*-chlorobenzaldehyde and *p*-anisaldehyde, as well as the diphenylmercaptal of the former, were found to be uncrystallizable oils and were not further investigated. The diphenylmercaptal of benzaldehyde, previously reported by Laves, *Ber.*, **25**, 355 (1892), to be an oil, forms colorless needles melting at 52°.

TABLE II

PRODUCTS FROM MERCAPTALS, FORMALDEHYDE AND HYDROGEN CHLORIDE IN BOILING ACETIC ACID

Original mercaptal	Product^{a} m. p., °C.	Analysis, % C	H	Miscellaneous	Remarks
Formaldehyde-diphenyl	181–184 (250)^{b}	65.8	5.3	...	Shows double m. p.
Benzaldehyde-diphenyl	192–195 (250)^{b}	66.7	5.6	...	Shows double m. p.
m-Nitrobenzaldehyde-diphenyl	192–195 (250)^{b}	66.6	5.6	N absent	Shows double m. p.
Benzaldehyde-di-*p*-nitrophenyl	183^{c}	48.7	3.4	N present	Mol. wt. in dioxane 318^{f}
Benzaldehyde-di-*p*-tolyl	183–184^{d}	70.2	6.13	S, 24.8	Mol. wt. in Bz 286^{f}
Formaldehyde-di-*p*-tolyl^{h}	186^{e}	70.6	6.18	...	Mol. wt. in Bz 284;^{f} mixed m. p. with previous product, 183°^{g}
m-Nitrobenzaldehyde-di-*p*-tolyl	180–181^{d}	..	..	N absent	Cryst. with difficulty
2-Brom-5-hydroxybenzaldehyde-di-*p*-tolyl	179^{d}	..	..	Br absent	Reaction slow; 10 hrs. boiling required
Benzophenone-diphenyl	No reaction				

[a] Weight of product obtained was about one-third to two-thirds the weight of mercaptal taken. [b] Colorless microcrystalline powder from dioxane. [c] Yellow plates from acetic acid. [d] Colorless prisms from acetic acid. [e] Colorless prisms from ethyl alcohol. [f] B. p. method using Menzies–Wright apparatus. [g] Approximate 1:1 mixture. [h] Reaction carried out at room temperature; inserted here for comparison with previous experiment.

acetic acid, 4 cc. of 40% aqueous formaldehyde added, and the clear solution saturated with hydrogen chloride. The mixture was then heated to gentle boiling in a 100-cc. side-neck flask fitted with a ground-on reflux condenser. A very slow current of hydrogen chloride was passed into the side-neck of the flask during the refluxing, which was continued until no further precipitate formed. This required from three to six hours in most cases, the product separating more completely on cooling. After filtering and washing, the product was recrystallized from glacial acetic acid, or dioxane in the case of less soluble materials. Table II gives data on eight experiments of this kind, involving seven mercaptals and one mercaptole.

Summary

1. Aromatic mercaptals have been found to undergo an apparent condensation reaction with formaldehyde in the presence of acetic acid and hydrogen chloride.

2. The crystalline products of this reaction given by eight different mercaptals have been described, and the possible nature of the reaction discussed.

3. Benzophenone diphenylmercaptole has been found to be unreactive under the conditions studied.

4. Five new crystalline mercaptals have been prepared and characterized.

PRINCETON, NEW JERSEY RECEIVED FEBRUARY 27, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

Quinazolines. VII. The Interaction of 2,4-Dichloroquinazoline in Alcohol with Ammonia and with Methylamine

BY EDW. VOPICKA AND N. A. LANGE

The interaction of 2,4-dichloroquinazoline with ammonia and with methylamine received a very brief mention in a paper by Kötz[1] which he termed a preliminary report and in which he reserved the field to himself. A search of the literature to date does not disclose any further work with these reactions. Because of certain studies on the reaction of 2,4-dichloroquinazoline with aniline and other bases[2] it seemed desirable to repeat Kötz' work and to determine with more certainty just what products were formed.

When 2,4-dichloroquinazoline in alcohol is heated with ammonia or with methylamine, hydrochlorides of the monobasic diamines, 2,4-diaminoquinazoline and 2,4-dimethylaminoquinazoline, respectively, are formed. The corresponding free bases are readily obtained from their hydrochlorides by treatment with sodium alcoholates; they are colorless, easily soluble substances, crystallizing in needles, and forming characteristic salts. These two diaminoquinazolines and their salts show certain similarities to 2,4-dianilinoquinazoline:[2] like the dianilino derivative they are both monobasic as regards salt formation;

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[1] Kötz, *J. prakt. Chem.*, [2] **47**, 303 (1893).

[2] Lange and Sheibley, THIS JOURNAL, **53**, 3871 (1931).