ably is carried over by the nitrogen stream. That being the case, the milliequivalents of iodine consumed will be

$$\text{meq. } \mathrm{I_2} = \text{mmoles RSH} + 2\text{x}(\text{mmoles } \mathrm{HSO_3^-})$$

Assuming that all EtSOH formed in equation 7 reacts by 8,[19] the amount of sulfate formed in the original solution will be

$$\text{mmoles } \mathrm{SO_4^{-2}} = \text{mmoles RSH} + \text{mmoles } \mathrm{HSO_3^-}$$

From this the fraction of the Bunte salt disappearing by reactions 3 and 7, α, is

$$\alpha = \frac{\text{mmoles } \mathrm{HSO_3^-}}{\text{mmoles } \mathrm{SO_4^{-2}}} = \frac{\text{meq. } \mathrm{I_2} - \text{mmoles } \mathrm{SO_4^{-2}}}{\text{mmoles } \mathrm{SO_4^{-2}}}$$

Two runs gave the following results for mmoles $\mathrm{SO_4^{-2}}$, meq. $\mathrm{I_2}$, α: (1) 5.36, 5.65, 0.05; (2) 2.68, 2.76, 0.03.

In run 1, instead of ethanolic iodine, aqueous iodine overlayered with a small amount of pentane was used in trap C. After titration of the excess iodine the pentane solution was diluted to known volume and its diethyl disulfide content determined by v.p.c. comparison with standard solutions of the disulfide in pentane. The amount of disulfide formed should be

$$\underset{\text{in trap}}{\text{mmoles } \mathrm{R_2S_2}} = \frac{\text{moles RSH}}{2} = \frac{2 \text{ mmoles } \mathrm{SO_4^{-2}} - \text{meq. } \mathrm{I_2}}{2}$$

The value calculated in this way is 2.53 mmoles. The amount actually found in the pentane solution was 2.48 mmoles.

Procedure for Kinetic Runs.—The same apparatus and procedure was used for the kinetic runs, except that, instead of an excess of iodine, only a small aliquot of iodine was added initially. The time required for the iodine color to fade was noted, another aliquot was added, and the procedure was repeated as many times as desired. Finally an excess of standard iodine was added, and after a suitable length of time, the "infinity" consumption of iodine was determined. This is the same type of procedure used before to follow the thiolsulfonate decompositions.[18]

Acknowledgment.—This work was aided by a grant from the Alfred P. Sloan Foundation.

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[19] Alternate assumptions such as disproportionation ($2\mathrm{EtSOH} \rightarrow \mathrm{EtSH} + \mathrm{EtSO_2H}$) lead to smaller values for α, the fraction of the Bunte salt *not* reacting by equation 1.

The Metalation and Alkylation of Mercaptals

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The formation of a mercaptal anion and its reaction with various alkylating and acylating agents was studied. The conversion of the alkylated and acylated products into carbonyl compounds can serve as a source of monoketones, α-diketones, acylions, α-keto esters, and β-keto esters. A new desulfurizing system is discussed.

For many years it was generally believed that mercaptals, like their oxygen analogs, were stable to alkali.[1a-c] Recent reports, however, have shown that with a sufficiently powerful base the hydrogen is labile. Arens[2] and co-workers treated formaldehyde diethylmercaptal (I) with sodium amide in liquid ammonia followed by an alkyl halide and obtained II. The 3d-orbital overlap between a sulfur atom and the adjacent carbanion and the inductive effect of the two mercapto groups were put forth as explanations for the stability of the carbanion. Furthermore, Oae, Ohno, and Tagaki[3] have shown that acrolein diethylmercaptal (III) was isomerized by potassium t-butoxide to the ketene mercaptal IV.

$$\underset{\mathrm{I}}{\mathrm{CH_2(SC_2H_5)_2}} \xrightarrow[\mathrm{NH_3}]{\mathrm{NaNH_2}} \mathrm{\bar{C}H(SC_2H_5)_2} \xrightarrow{\mathrm{RX}} \underset{\mathrm{II}}{\mathrm{RCH(SC_2H_5)_2}}$$

$$\underset{\mathrm{III}}{\mathrm{CH_2{=}CHCH(SC_2H_5)_2}} \xrightarrow{\overset{+}{\mathrm{K}}\bar{\mathrm{O}}\mathrm{C(CH_3)_3}} \underset{\mathrm{IV}}{\mathrm{CH_3CH{=}C(SC_2H_5)_2}}$$

The report[2] that a mercaptal reacts with a strong base to give an anion has opened up some interesting areas of mercaptal chemistry. Besides the inherent interest in metalation reactions, reaction of the anion with alkylating and acylating agents provides a synthetic route to a wide variety of functional groups, *e.g.*, hydrolysis of the products leads to carbonyl compounds, whereas desulfurization reduces the mercaptole function to a methylene group.

We have studied the metalation of benzaldehyde diphenylmercaptal (V) with various bases and wish to report our results. Alkali metal amides in liquid ammonia proved unsatisfactory for metalation in this system because of undesirable side reactions. Potassium t-butoxide in t-butyl alcohol apparently did not form the anion, as starting material was recovered after treatment with an alkyl halide. Potassium t-butoxide in anhydrous tetrahydrofuran gave a low yield (25%) of alkylated product; the low yield can probably be accounted for by the unfavorable alcohol–mercaptal equilibrium. Organometallic bases such as Grignard reagents, phenyllithium, or n-butyllithium are unsatisfactory metalating agents because they have been reported to cleave mercaptals.[4,5]

$$\underset{\mathrm{V}}{\mathrm{C_6H_5CH(SC_6H_5)_2}} + \mathrm{KOC(CH_3)_3} \rightleftarrows \underset{\mathrm{VI}}{\mathrm{C_6H_5\bar{C}(SC_6H_5)_2}} + \mathrm{(CH_3)_3COH}$$

$$\mathrm{RCH(SR)_2 + R'M \longrightarrow RCHR'(SR) + RSM}$$

Sodium hydride dispersion in ether, tetrahydrofuran or benzene gave very little evolution of hydrogen when treated with benzaldehyde diphenylmercaptal (V). Sodium hydride dispersion in the dimethyl ether of ethylene glycol or the dimethyl ether of diethylene glycol required a high reaction temperature before the evolution of hydrogen began and led to extensive decomposition. However, an excellent solvent for such

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[1] (a) O. Behagel and H. Ratz, *Ber.*, **72**, 1257 (1939); (b) D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 67 (1951); (c) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1960, p. 331.

[2] J. F. Arens, M. Froling, and A. Froling, *Rec. trav. chim.*, **78**, 663 (1959).

[3] S. Oae, A. Ohno, and W. Tagaki, *Chem. Ind.* (London), **7**, 304 (1962).

[4] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1960, p. 332.

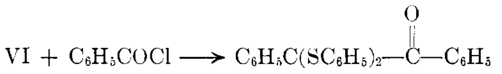
[5] A. Schonberg, *et al.*, *Ber.*, **64**, 2577 (1931).

metalations was dimethylformamide. Both the mercaptal (colorless in dimethylformamide) and its sodium salt (reddish orange solution) were extremely soluble in dimethylformamide and the rate of metalation could be followed by measuring the evolved hydrogen. The metalations were run at 0° to minimize attack of the anion on dimethyl formamide, which was found to occur at room temperature. After one hour at room temperature dimethylamine was detected in the effluent gas and the reaction mixture turned black. However, at 0°, after an equivalent amount of hydrogen was evolved, benzaldehyde diphenylmercaptal (V) was regenerated quantitatively by treatment with water.

The reaction of the anion of benzaldehyde diphenylmercaptal (VI) with several alkylating and acylating agents was investigated. The reaction of the anion with methyl iodide afforded a good yield of VII. The product was identical to that prepared from acetophenone and benzenethiol.[6]

$$\underset{\text{VI}}{C_6H_5\bar{C}(SC_6H_5)_2} + CH_3I \longrightarrow \underset{\text{VII}}{C_6H_5C(SC_6H_5)_2CH_3}$$

The anion VI also reacted with benzoyl chloride, ethyl chlorocarbonate, and ethyl bromoacetate to produce VIII, IX, and X, respectively. The yields were low because of a competing reaction with the solvent, dimethylformamide.[7,8]



$$VI + C_6H_5COCl \longrightarrow C_6H_5C(SC_6H_5)_2\text{—}\overset{O}{\overset{\|}{C}}\text{—}C_6H_5$$

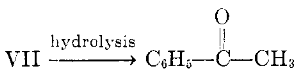
VIII

$$VI + Cl\text{—}CO_2C_2H_5 \longrightarrow \underset{\text{IX}}{C_6H_5C(SC_6H_5)_2CO_2C_2H_5}$$

$$VI + BrCH_2CO_2C_2H_5 \longrightarrow \underset{\text{X}}{C_6H_5C(SC_6H_5)_2CH_2CO_2C_2H_5}$$

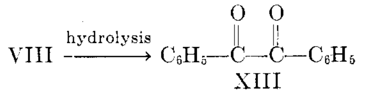
In dimethylformamide both benzoyl chloride and ethyl chlorocarbonate form solutions which are conducting. With benzoyl chloride various proposals have been made for the structure of the salt formed, but these are only tentative.[7] Although this salt reacted with both water and aniline to form benzoic acid and benzanilide, respectively, it did not react with anion VI at 0° at a convenient rate. Heating the reaction mixture to reflux temperature for 30 minutes led to a low yield (38%) of VIII and appreciable decomposition. When the salt formed from benzoyl chloride was refluxed for four hours, an almost quantitative yield of dimethyl benzamide was formed.[8] Attempts to find a more suitable solvent for acylations were unsuccessful.

Each of these products (VII, VIII, IX, X) could be hydrolyzed to the corresponding carbonyl compound in excellent yield. The general utility of these reactions is illustrated by the equations below.



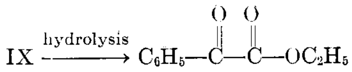
$$VII \xrightarrow{\text{hydrolysis}} C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3$$

XII



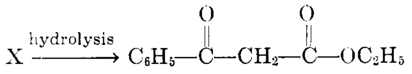
$$VIII \xrightarrow{\text{hydrolysis}} C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}C_6H_5$$

XIII



$$IX \xrightarrow{\text{hydrolysis}} C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}OC_2H_5$$

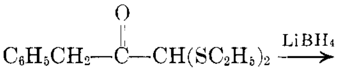
XIV



$$X \xrightarrow{\text{hydrolysis}} C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_2\text{—}\overset{O}{\overset{\|}{C}}\text{—}OC_2H_5$$

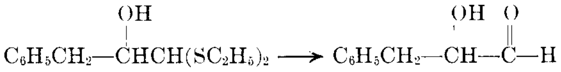
XV

For compounds such as VIII and IX the hydrolysis method of Weygand[9] was most convenient. The method involved treatment of the mercaptole in an acetic acid–water mixture using the dropwise addition of bromine to oxidize the benzenethiol to disulfide and thereby shift the equilibrium. This method gave yields of 80–90% (calculated on the basis of the amount of carbonyl compound isolated). Weygand also reported the reduction of XI with lithium borohydride, followed by hydrolysis to yield XVI, which could also be hydrolyzed by this method to give XVII.



$$C_6H_5CH_2\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH(SC_2H_5)_2 \xrightarrow{LiBH_4}$$

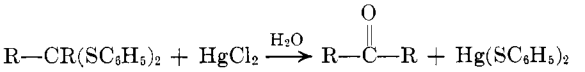
XI



$$C_6H_5CH_2\text{—}\overset{OH}{\overset{|}{C}}HCH(SC_2H_5)_2 \longrightarrow C_6H_5CH_2\text{—}\overset{OH}{\overset{|}{C}H}\text{—}\overset{O}{\overset{\|}{C}}\text{—}H$$

XVI XVII

With compounds VII and X, which will react with bromine under acidic conditions, the mercuric chloride cleavage of mercaptoles was employed.[10] In this method the hydrolysis product, benzenethiol, reacts with mercuric chloride to form an insoluble mercuric mercaptide. This method has been applied extensively in the sugar series with excellent yields.[11,12]



$$R\text{—}CR(SC_6H_5)_2 + HgCl_2 \xrightarrow{H_2O} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}R + Hg(SC_6H_5)_2$$

Raney nickel desulfurization of mercaptals and mercaptoles is a standard synthetic method for reducing carbonyl functions to methylene or methyl groups.[13,14] Newman and Walborsky[15] reported the reduction of the methylmercaptoles of XIV and XV in 78% yield using Raney nickel. One disadvantage of this method is the preparation of Raney nickel and its deactivation on aging. It is also difficult to determine accurately the weight of nickel used because of the necessity of keeping the pyrophoric solid wet.

A more convenient method for the desulfurization of mercaptoles is to treat a specific amount of nickel (II) chloride with an excess of sodium borohydride. The borohydride reduces the nickel and this catalyzes the hydrolysis of the borohydride,[16,17] thus generating a large amount of hydrogen in the presence of finely divided nickel. The nickel so obtained has hydrogen adsorbed on its surface and is capable of reducing carbon–sulfur bonds. The procedure is simple and by varying the amounts of nickel(II) chloride and sodium borohydride, a certain amount of selectivity can be ob-

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(6) E. Campaigne and J. R. Leal, *J. Am. Chem. Soc.*, **76**, 1272 (1954).

(7) H. K. Hall, *ibid.*, **78**, 2717 (1956).

(8) G. M. Coppinger, *ibid.*, **76**, 1372 (1954).

(9) F. Weygand and H. J. Bestmann, *Ber.*, **90**, 1230 (1957).

(10) J. English, Jr., and P. H. Griswald, Jr., *J. Am. Chem. Soc.*, **67**, 2039 (1945).

(11) M. L. Wolfrom, *ibid.*, **51**, 2188 (1929).

(12) H. L. Arnold and W. L. Evans, *ibid.*, **58**, 1950 (1936).

(13) M. L. Wolfrom and J. V. Karabinos, *ibid.*, **66**, 909 (1944).

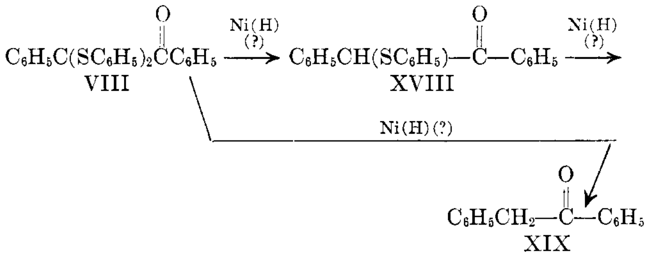
(14) H. Hauptman, *ibid.*, **69**, 562 (1947).

(15) M. S. Newman and H. Walborsky, *ibid.*, **72**, 4296 (1950).

(16) H. L. Schlesinger, *et al.*, *ibid.*, **75**, 215 (1953).

(17) H. C. Brown and C. A. Brown, *ibid.*, **84**, 1493 (1962).

tained. For example, 0.02 mole of nickel(II) chloride hexahydrate dissolved in ethanol and treated with an equimolar amount of sodium borohydride gave a vigorous reaction and the immediate formation of a finely divided black solid. After a short time the diphenylmercaptole of benzil, VIII, was added and the solution was refluxed for twelve hours. The compound isolated on work-up was α-phenylmercaptodesoxybenzoin (XVIII) in 70% yield. This compound, treated with additional nickel reagent under exactly the same conditions, gave phenyl benzyl ketone (XIX), identified by its melting point and its 2,4-dinitrophenylhydrazone. The diphenylmercaptole VIII was also reduced directly to phenyl benzyl ketone in 60% yield by using a ten to one mole ratio of nickel to mercaptole.



$$C_6H_5C(SC_6H_5)_2\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow[(?)]{Ni(H)} C_6H_5CH(SC_6H_5)-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow[(?)]{Ni(H)} C_6H_5CH_2-\overset{O}{\overset{\|}{C}}-C_6H_5$$

Experimental[18]

Preparation of Benzaldehyde Diphenylmercaptal.—In a 1-l. round-bottom three-neck flask fitted with a reflux condenser, mechanical stirrer, and a 100-ml. addition funnel, were placed 500 ml. of glacial acetic acid, 20 g. of anhydrous zinc chloride, and 20 g. (0.2 mole) of benzaldehyde. To this was added dropwise 44.5 g. (0.4 mole) of benzenethiol with stirring. The reaction was stirred for 12 hr. at room temperature and then heated on a steam bath for 1 hr. On cooling, 21 g. of white crystals was filtered off. To the filtrate was added 50 ml. of water. After cooling in ice, light tan crystals (31 g.) were filtered off and recrystallized from pentane, m.p. 52–53° (lit.,[19] 48.5–51.5°). The total weight isolated was 52 g. (83%).

Sodium Hydride Determination.—A 25% sodium hydride dispersion obtained from Callery Chemical Co., was found to be the most efficient form of sodium hydride for these metalations. In an oven-dried flask fitted with reflux condenser and dropping funnel, was placed 3 ml. of dispersion. The outlet of the condenser was connected to a wet test gas meter. Wet ether was added cautiously from the dropping funnel. The volume of the gas liberated was corrected to standard conditions and the percentage sodium hydride was calculated from this.

Purification of Dimethylformamide.—The dimethylformamide was dried over calcium hydride and then distilled from calcium hydride before use.

Acetophenone Diphenylmercaptole.—Five grams (0.016 mole) of benzaldehyde diphenylmercaptal was dissolved in 20 ml. of dry dimethylformamide. The mixture was cooled to 0°. Ten milliliters of sodium hydride dispersion (0.02 mole) was added and the mixture stirred and kept at 0° until hydrogen evolution had ceased. To this solution was added dry methyl iodide (slight excess) and the reaction mixture was stirred for 6.5 hr. There was a color change from reddish orange to very pale yellow during this period. The reaction mixture was poured into ice–water and stirred vigorously for a short time to destroy any residual sodium hydride. The water solution was extracted three times with chloroform and then the chloroform solution was extracted three times with water to remove any remaining dimethylformamide. The chloroform solution was then dried by treatment first with anhydrous calcium chloride and then with anhydrous calcium sulfate. The chloroform was removed under reduced pressure to give a yellow oil. The yellow oil was chromatographed on a 2.3 cm. × 38 cm. column using acid-washed alumina (Merck) and pentane (35–37°) as eluent. Fractions were collected in 200-ml. portions. The first fraction contained only the 10 ml. of hydrocarbon oil used in sodium hydride dispersions. Fractions 2 to 6 contained 3.2 g. of acetophenone diphenylmercaptole, m.p. 54–55° (63%).

Benzil Diphenylmercaptole (VIII).—The anion was prepared as described above from 12.6 g. of benzaldehyde diphenylmercaptal and 30 ml. of sodium hydride dispersion. To a solution of the anion at 0° was added 7.4 g. of redistilled benzoyl chloride. An immediate color change from reddish orange to bright yellow occurred. The reaction mixture was refluxed for 30 min., cooled and the dark solution was poured into water. The resulting mixture was stirred vigorously to destroy any residual sodium hydride and was extracted with chloroform. The chloroform solution was washed with water and dried over calcium chloride. The solvent was removed under reduced pressure and the dark oil (43 g.) was chromatographed on a 2.3 cm. × 38 cm. column of acid-washed alumina (Merck) using pentane (35–37°) as eluent. Fraction 1 contained 13 ml. of the hydrocarbon oil used in sodium hydride dispersions. Fractions 3–5 contained starting material (1.3 g.), and fractions 6–9 contained 2.0 g. of phenyl thiolbenzoate [m.p. 55–56° (lit.,[20] 55–56°), infrared 6.0 μ (C=O), and hydrolyzed by dilute aqueous alkali to benzoic acid and benzenethiol]. Fractions 10–15 contained 5.2 g. of the expected product (VIII) (38%). The white solid was recrystallized from ethanol, m.p. 138–139°. This material was identical to that formed by condensing benzenethiol with benzil in the presence of boron trifluoride etherate.

Anal. Calcd. for $C_{26}H_{20}OS_2$: C, 75.71; H, 4.89; S, 15.52. Found: C, 75.86: H, 5.00; S, 15.45.

Ethyl Benzoylformate Diphenylmercaptole (IX).—The anion was prepared in the manner described above from 12.6 g. of benzaldehyde diphenylmercaptal. After the evolution of hydrogen had ceased 6.0 g. of redistilled ethyl chlorocarbonate was added. There was an immediate color change to bright yellow but no precipitation of sodium chloride (sodium chloride has a very low solubility in dimethylformamide). The mixture was refluxed for 30 min. and then poured onto ice. The water solution was extracted with chloroform. The chloroform solution was extracted with water to remove any remaining dimethylformamide. The solution was dried over anhydrous calcium chloride and the solvent removed under reduced pressure. The residue was then taken up in 50 ml. of glacial acetic acid. To this solution was added 1.0 ml. of concentrated hydrochloric acid and 7.0 ml. of water. The mixture was warmed to 50° on the steam bath. Bromine, 25.6 g. (0.16 mole), dissolved in 75 ml. of glacial acetic acid, was added slowly. After complete addition (45 min.) the mixture was allowed to stand at room temperature for 8 hr. The mixture was poured into water and extracted with chloroform. The chloroform extracts were combined and washed with saturated sodium carbonate solution, water and dried over calcium chloride. The solvent was removed under reduced pressure and the residue subjected to vacuum distillation. A small forerun of 1.5 g. of benzaldehyde was isolated (2,4-dinitrophenylhydrazone, m.p. 237–238°, lit.,[21] 237–238°). Pure ethyl benzoylformate (2,4-DNP, m.p. 163–164°, lit.,[21] 163°) distilled over at 104–105° at 4 mm.; 1.8 g. (25%). The pot residue consisted of phenyl disulfide, m.p. 59–60°; its infrared spectrum was superimposable on that of an authentic sample.

Ethyl Benzoylacetate Diphenylmercaptole (X).—The anion of benzaldehyde diphenylmercaptal was prepared from 12.6 g. of mercaptal as described above. To this solution at 0° was added 6.8 g. (slight excess) of ethyl bromoacetate. The reaction mixture was refluxed for 30 min. and worked up in the same manner as described above. However, the dark oil obtained was not chromatographed but taken up in methanol. On standing a white solid crystallized, m.p. 86–88°. The solid was recrystallized from methanol, m.p. 90–91° (lit.,[6] 91–92°); weight 2.7 g. The mother liquors were evaporated to dryness and the residue chromatographed on acid-washed alumina (Merck) using pentane as eluent. Three grams of benzaldehyde diphenylmercaptal was recovered from the column.

Hydrolysis of Benzil Diphenylmercaptol (VIII).—To a solution of 4.1 g. of benzil diphenylmercaptole in 50 ml. of glacial acetic acid was added 10 ml. of 15% hydrochloric acid. The mixture was warmed on the steam bath to 50° and treated dropwise with 16 g. of a 20% solution of bromine in acetic acid. The bromine

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

[19] M. M. Campos and H. Hauptman, *J. Am. Chem. Soc.*, **74**, 2962 (1952).

[20] O. Schiller, *Ber.*, **9**, 1635 (1876).

[21] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Determination of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 318.

color disappeared very rapidly. After the addition was complete the mixture was heated on a steam bath for 1 hr. and let stand at room temperature for 18 hr. The solvent was removed under reduced pressure and the residue was taken up in chloroform, dried over calcium chloride, filtered, and evaporated. The light yellow oil was chromatographed on a 2.3 × 38 cm. column with acid-washed alumina (Merck) using pentane as eluent. The first fraction contained phenyl disulfide contaminated with a small amount of benzil. This was recrystallized from alcohol, m.p. 60–61° (lit.,[22] 60–61°). There was 1.20 g. of phenyl disulfide representing a yield of 55%. The second and third fraction contained benzil (1.7 g., 85%), m.p. 93–94°,2, 4-DNP, m.p. 187–189°, 2,4-DNP, m.m.p. 187–189°.

Selective Desulfurization of Benzil Diphenylmercaptole (VIII) with Nickel.—The nickel catalyst was prepared as follows: To 4.8 g. (0.02 mole) of nickel(II) chloride hexahydrate in ethanol was added in small portions 0.75 g. (0.02 mole) of sodium borohydride. There was an immediate precipitation of a finely divided black solid. The evolution of hydrogen was brisk. The mixture was stirred for 30 min. and 4.1 g. (0.01 mole) of benzil diphenylmercaptole was added. The mixture was refluxed for 12 hr. and cooled. The solution was filtered through a sintered glass funnel and the solvent removed under reduced pressure. The residue was recrystallized from ethanol to give 2.2 g. (71%) of α-phenylmercaptodesoxybenzoin as white crystals, m.p. 78–79° (lit.,[23] 81°). Infrared spectrum in chloroform shows a strong carbonyl absorption at 5.95 μ. The spectrum of XVIII differed from that of VIII in several respects. Further confirmation of the structure of XVIII was obtained by treating it with additional nickel reagent under like conditions to obtain phenyl benzyl ketone (XIX).

Complete Desulfurization of Benzil Diphenylmercaptole with Nickel.—The reaction was run in the same manner as described above except the ratio of nickel(II) chloride and borohydride to VIII was raised to ten to one. After filtration of the nickel and evaporation of the solvent, 1.2 g. (61%) of phenyl benzyl ketone (XIX), m.p. 55–56° (lit.,[24] 55–56°), 2,4-DNP, m.p. 201–203° (lit.,[21] 204°), was isolated.

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[22] H. Hubner and J. Alsberg, *Ann.*, **156**, 307 (1870).

[23] W. A. Mitchell and S. Smiles, *J. Chem. Soc.*, 1529 (1933).

[24] C. F. H. Allen and W. E. Barker, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 156.

The Intramolecular Cleavage of γ-Alkylmercaptobutyryl Chlorides

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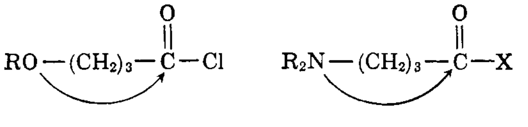
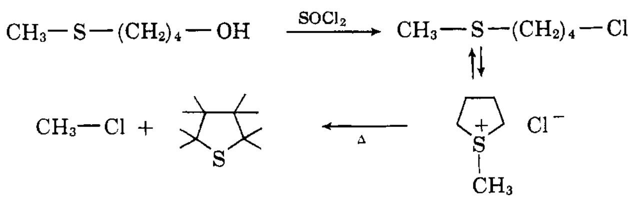
Compounds of the general structure, $R—S—(CH_2)_3COCl$, were cleaved under reflux conditions to give γ-thiolbutyrolactone, alkyl halide (R-Cl), and olefin (isolated when R = 2-octyl). As R was varied from primary to secondary to tertiary alkyl, the yield of thiolactone increased and less vigorous conditions were needed for reaction. When R was the *d*-2-octyl group, the resulting 2-octyl chloride showed net inversion.

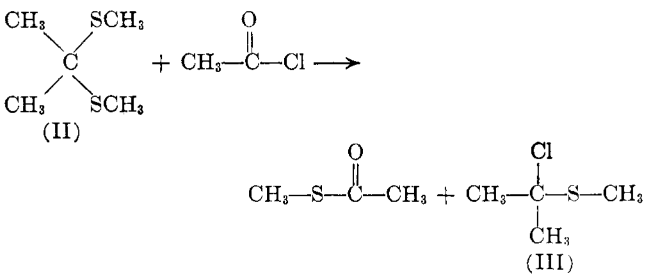
The intramolecular interactions of the elements, oxygen and nitrogen, with acyl chlorides or carboxylic anhydrides have been demonstrated.[2] Furthermore, in attempts to prepare 1-chloro-4-methylthiobutane from the corresponding alcohol by treatment with thionyl chloride, the sulfonium chloride (I) was obtained, which was pyrolyzed to tetrahydrothiophene.[3] In fact, cyclic sulfonium salts and their degradations have been well studied.[4] Bohme[5] and co-workers have studied the cleavage of mercaptals by acyl chlorides, *e.g.*, treatment of II with acetyl chloride gave methyl thiolacetate and III. Likewise, simple sulfides have been cleaved by acyl bromides and iodides.[6] While thioethers are cleaved by acyl iodides,[6c] the rate of cleavage is very much slower than that of the analogous ethers. The cleavage products from diethyl sulfide and acetyl iodide were ethyl iodide and ethyl thiolacetate. These authors also found that acetyl chloride without catalysts failed completely to cleave diethyl sulfide after seven days at 100°.



(X = chloro and acetoxy)



I



The purpose of this investigation was to determine if sulfur would participate intramolecularly with an

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