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α,β -Unsaturated Sulfides. The Reaction of Thiophenol with Certain Ketones¹

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The reaction between thiophenol and certain ketones, under the conditions which would be expected to form mercapitals. has been found to yield unsaturated sulfides. Of the ketones investigated, 5,5-dimethyl-1,3-cyclohexanedione, propio-phenone, desoxybenzoin and isobutyrophenone gave unsaturated sulfides, while acetophenone and ethyl benzoylacetate gave mercaptals. Pivalophenone did not react with thiophenol. Benzyl mercaptan and 2-methyl-1-indanone yielded benzyl 2-methyl-3-indenyl sulfide. A reaction mechanism is discussed.

Introduction

The reaction between a ketone and a thiol in the presence of an acid catalyst generally leads to the formation of a mercaptal, 3 although scattered reports in the literature indicate that certain cyclic ketones yield unsaturated sulfides (enol thioethers) rather than the expected mercaptals. Thus 4cholesten-3-one⁴ and other 3-ketosteroids unsaturated at position 4 are reported⁵ to give α,β -unsaturated sulfides when reacting with excess thiol in the presence of anhydrous sodium sulfate and zinc chloride. A similar behavior is claimed for 1,3cyclohexanediones6 which form 3-alkylthio-2-cyclohexanones when treated with thiols in the presence of hydrogen chloride. Finally, it was observed7 that 2-methyl-1-indanone and 2-methyl-1-tetralone react with thiophenol under the conditions of the mercaptal reaction to produce phenyl 2methyl-3-indenyl sulfide and phenyl 2-methyl-3,4dihydro-1-naphthyl sulfide, respectively, and not the corresponding mercaptals.

Inasmuch as the cases cited above represent exceptions to a general reaction of very wide scope and few reported limitations, an investigation of the mercaptal reaction was initiated with the object of exploring the extent to which the anomalous unsaturated sulfide product occurs as well as to determine some of the factors which influence the formation of the unsaturated sulfides over that of the mercaptals.

Discussion

In order to determine whether the formation of the unsaturated sulfides observed previously⁷ was the result of the unstable nature of the mercaptals initially formed or of the low reactivity of the thiol used, 2-methyl-1-indanone was treated with benzyl mercaptan.8 In this case, the nature of the thiol did not appear to be the only factor involved in the formation of the α,β -unsaturated sulfide since benzyl 2-methyl-3-indenyl sulfide was obtained. Further support for this assumption was found in the fact that 5,5-dimethyl-1,3-cyclohexanedione formed

(1) Taken from a portion of the thesis submitted by Joseph R. Leal in partial fulfillment of the requirements for the degree Doctor of (2) Frederick Gardner Cottrell Fellow in Chemistry, 1951–1952.

(3) E. Baumann, Ber., 18, 883 (1885).

(4) S. Bernstein and L. Dorfman, THIS JOURNAL, 68, 1152 (1946).

(5) G. Rosenkranz, S. Kaufmann and J. Romo, ibid., 71, 3689 (1949).

(6) J. D. Kendall and F. P. Doyle, British Patent 595,783, Dec. 16, 1947 (C. A., 42, 4764 (1918)).

(7) E. Campaigne and R. D. Moss, THIS JOURNAL, 76, 1269 (1954). (8) Thiophenol represents the least reactive of the thiols in the

formation of mercaptals and forms the least stable mercaptals, benzyl mercaptan represents the most reactive thiol, forming the most stable mercaptals. Cf. T. Posner, Ber., 34, 2643 (1901).

unsaturated sulfides with ethanethiol⁶ as well as with thiophenol. In other cases, however, the thiol apparently influences the course of the reaction. For example, benzyl mercaptan and 1,2-ethanedithiol yield mercaptals with 4-cholesten-3-one,9 whereas thiophenol yields an unsaturated sulfide.4

With respect to the nature of the ketone, it can be postulated that steric hindrance about the carbonyl function is the factor responsible for the new course of the mercaptal reactions.¹⁰ On the other hand, although 2-methyl-1-indanone formed unsaturated sulfides with thiophenol and benzyl mercaptan, 2,3-diphenyl-1-indenone is reported to form the dibenzyl mercaptal,¹¹ and fluorenone the diphenyl mercaptal.¹² On the basis of steric hindrance alone, these compounds might be expected to form only hemimercaptals or not react at all.

In order to elucidate the role of the ketone in the mercaptal reaction, a series of phenones I reacted with thiophenol under conditions which usually lead to mercaptal formation. In this series acetophenone (Ia) and ethyl benzoylacetate (Ib) gave the corresponding diphenyl mercaptals (IIa,b) while propiophenone (Ic), desoxybenzoin (Id) and isobutyrophenone (Ie) furnished unsaturated sulfides III.



Pivalophenone did not react with thiophenol. Construction of a Fisher-Hirschfelder model of pivalophenone suggested that although a hemimercaptal of pivalophenone could possibly be formed, the introduction of a second phenylthio group was highly unlikely.

The fact that ethyl benzoylacetate formed a mercaptal with thiophenol is in agreement with the results obtained with ethyl acetoacetate and other β -keto esters.^{13,14} Hydrolysis of the mercaptal es-

(9) H. Hauptmann, THIS JOURNAL, 69, 562 (1947).

(10) Such an explanation has been suggested for the failure of 11-keto steroids to react with thiols, H. Hauptmann and M. Campos, ibid., 74, 3179 (1952).

- (11) A. Schönberg and O. Schütz, Ber., 60, 2344 (1927).
- (12) A. Schönberg and T. Stolpp, Ann., 483, 90 (1930).
- (13) R. Escales and E. Baumann, Ber., 19, 1787 (1886).
- (14) T. Posner, ibid., 32, 2801 (1899).

ter resulted in the loss of one molecule of thiophenol, a behavior which appears to be characteristic of this type of mercaptal.^{13,14} Although the mercaptal ester, ethyl β , β -bis-(phenylthio)-hydrocinnamate, was not found reported in the literature, the other possible reaction product, ethyl β -phenylthiocinnamate, is reported.¹⁵ Inasmuch as the melting point of the mercaptal ester IIb (92-93°) and that of the reported unsaturated sulfide ester (95-96°) lay close together, some doubt existed as to the identity of the product obtained from the benzoylacetate and thiophenol. Furthermore, the melting point of the acid obtained by hydrolysis of the mercaptal ester (192°) was much higher than that reported in the literature¹⁵ for the acid obtained by hydrolysis of the unsaturated sulfide ester (162°) , although the elemental analysis indicated that the compositions of the two acids were identical. Ethyl β -phenylthiocinnamate was prepared and found to depress the melting point of the mercaptal ester. Upon hydrolysis, the unsaturated sulfide ester yielded an acid melting at 162°, which depressed the melting point of the acid obtained from the mercaptal ester. The two acids probably represent the *cis* and *trans* isomers of β -phenylthiocinnamic acid.

Because ethyl β , β -bis-(phenylthio)-hydrocinnamate and β -phenylthiocinnamic acid have certain structural similarities, differences in their infrared absorption spectra should be attributable principally to their specific structural differences. Although the two curves were quite similar, the acid curve showed absorption bands at 5.93 μ , assigned to a conjugated carbonyl group¹⁶ and at 7.12 μ , assigned to a carbon–carbon double bond,¹⁷ which were absent in the ester curve. The ester curve had an absorption band at 5.73 μ , assigned to an ester carbonyl group, one at 7.32 μ , assigned to an ethyl group, and one at 8.68 μ , assigned to a methylene group.¹⁶ Absorption bands at 14.47 μ , assigned to the sulfide linkage,¹⁸ occurred in both curves.

The reaction product isolated from thiophenol and desoxybenzoin could be fractionally crystallized into two fractions having sharp melting points. Analysis of the two fractions indicated that both had the same elementary compositions, corresponding to that required for phenylthiostilbene (IIId). On the basis of the analyses and their very similar solubility behavior, the two fractions very likely represent the *cis* and *trans* isomers of phenylthiostilbene, but attempts at interconversion were unsuccessful.

Attempts to oxidize the sulfides obtained in this study to sulfones generally failed,¹⁹ although ben-

(15) S. Ruhemann and H. E. Stapleton, J. Chem. Soc., 77, 1179 (1900).

(16) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

(17) M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 492.

(18) Private communication from F. C. Nachod, Sterling-Winthrop Research Institute.

(19) The group RS—C==C— is reported to be highly susceptible to acid attack and nucleophilic replacement (D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951)). Mercaptals containing large alkyl or aryl groups yield mainly water-soluble sulfonic acids upon oxidation (C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 735). zyl 2-methyl-3-indenyl sulfide and phenyl 1-phenyl-1-propenyl sulfide (IIIc) furnished small yields of the corresponding sulfones. From ethyl β , β -bis-(phenylthio)-hydrocinnamate, a very small amount of a substance which analyzed correctly for ethyl β phenylsulfinylcinnamate was isolated.

The mechanism of the mercaptal reaction may be represented as involving the addition of one mole of thiol to form a hemimercaptal followed by elimination of water accompanied by coördination of the second mole of thiol and the eventual loss of a proton.²⁰ The anomalous reaction course in which

$$\begin{array}{c} O \\ RCH_{2}C - R^{1} + C_{6}H_{5}SH & \longleftrightarrow & RCH_{2} - C - R^{1} & +H^{+} \\ & & & \\ SC_{6}H_{5} & & -H^{+} \\ RCH_{2} - C - R^{1} & -H_{2}C \\ & & & \\ SC_{6}H_{5} & & +H_{2}O \end{array} \xrightarrow{} \begin{array}{c} OH \\ RCH_{2}C + H_{5}C \\ SC_{6}H_{5} \\ V \end{array}$$

$$\begin{array}{c} \operatorname{RCH}_{2}^{+}C - \operatorname{R}^{1} + C_{6}H_{5}SH \xrightarrow{}\\ \downarrow\\ SC_{6}H_{5} \end{array}$$

V

 $\begin{array}{c} HS\overset{+}{C}_{6}H_{5} \\ RCH_{2}\overset{-}{C}-R^{1} \xrightarrow{-H^{+}} RCH_{2}\overset{-}{C}-R^{1} \\ \downarrow \\ SC_{6}H_{5} \end{array} \xrightarrow{+H^{+}} RCH_{2}\overset{-}{C}-R^{1} \\ \begin{array}{c} SC_{6}H_{5} \\ SC_{6}H_{5} \end{array}$

unsaturated sulfides are formed probably proceeds by the same route up to the carbonium ion V. At this point, two factors apparently influence the next step in the reaction. One is steric and the other electronic. If the carbon holding the first thio group is hindered and, at the same time, R is an electron-releasing group, the carbonium ion V may be more readily stabilized by an electron shift than by coördination with the second molecule of thiol.

$$R \rightarrow - \overbrace{CH_{2}}^{+} \stackrel{+}{\underset{SC_{6}H_{5}}{\overset{+}{\longrightarrow}}} RCH = C - R^{1} + H^{+}$$

If, however, R is an electron-attracting group, the conditions for stabilization by an electron shift will be less favored. The two possible reaction routes, leading to a mercaptal or an unsaturated sulfide, are very likely competitive in nature, with the final outcome depending upon a proper balance of the steric and electronic factors.

The results obtained in this investigation are in accord with the mechanism proposed. Thus, although acetophenone yielded the diphenyl mercaptal, when methyl groups were substituted for hydrogens in acetophenone, unsaturated sulfides were formed. Apparently, the phenyl group acted as an electron-releasing group in the reaction of desoxybenzoin with thiophenol. When a hydrogen of acetophenone was replaced by the electron-attracting carbethoxy group, the mercaptal resulted. No reaction occurred with pivalophenone since its structure prohibited the stabilization of the inter-

(20) Cf. the mechanism of acetal formation, E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 215. mediate carbonium ion while steric hindrance prevented the normal mercaptal reaction.

The same mechanism may be extended to explain the abnormal reaction of ethanethiol and benzyl mercaptan with benzoin to form 1,2-dithiostil-bene derivatives.²¹ In contrast to Posner's mechanism,^{21a} which involved the formation of the normal mercaptal followed by replacement of the hydroxyl group by a third molecule of thiol to form an unstable intermediate trisulfide which then lost a molecule of thiol, the reaction may be more simply represented as

yielded yellow crystals of β -phenylthiocinnamic acid, melting at 160–163° dec.

Benzyl 2-Methyl-3-indenyl Sulfide .--- Anhydrous hydrogen chloride was passed into a mixture consisting of 6.6 g. 0.045 mole) of 2-methyl-1-indanone and 11 g. (0.09 mole) of benzyl mercaptan in 50 ml. of absolute ethyl alcohol. After 15 minutes, 20 g. of freshly fused zinc chloride was added to the reaction mixture and the flask shaken for 30 minutes. The reaction mixture was shaken intermittently but frequently for 2 hours, and then poured over ice, extracted with ether and the ether solution washed successively with water, aqueous sodium carbonate and water. Upon distillation of the dried ether solution, 9 g. (80%) of an oil, b.p. $165-170^{\circ}$ at 1.5 mm., was obtained which finally solidified after refrigeration and trituration with cold ethyl

$$\begin{array}{c} OH & O \\ C_{6}H_{5}CH - CC_{6}H_{5} & \underbrace{C_{6}H_{5}CH_{2}C_{6}H_{5}}_{C_{6}H_{5}CH - C(OH)C_{6}H_{5}} & \underbrace{H^{+/} - H_{2}O}_{VI} & OH & SCH_{2}C_{6}H_{5} & OH & SCH_{2}C_{6}H_{5} \\ VI & & & \\ VI & & & \\ VI & & & \\ VI & & \\ SCH_{2}C_{6}H_{5} & \underbrace{-H^{+}}_{C_{6}H_{5}C} - CHC_{6}H_{5} & \underbrace{H^{+/} - H_{2}O}_{C_{6}H_{5}C} - CHC_{6}H_{5} & \underbrace{-H^{-}}_{C_{6}H_{5}CH_{2}C_{6}H_{5}} & OH & SCH_{2}C_{6}H_{5} \\ OH & SCH_{2}C_{6}H_{5} & \underbrace{-H^{+}}_{SCH_{2}C_{6}H_{5}} & \underbrace{-H^{+}}_{C_{6}H_{5}C} - CHC_{6}H_{5} & \underbrace{-H^{+/} - H_{2}O}_{SCH_{2}C_{6}H_{5}} & OH & SCH_{2}C_{6}H_{5} \\ OH & SCH_{2}C_{6}H_{5} & \underbrace{-H^{+}}_{SCH_{2}C_{6}H_{5}} & \underbrace{-H^{+}}_{SCH_{2}C_{$$

The tendency for the intermediate carbonium ions VI and VIII to become stabilized by electron shifts, rather than coördination with another molecule of thiol, would be expected to be high, since such stabilization leads to structures which allow for resonance with the phenyl groups. The fact that 2methoxy-5-chlorothiophenol forms α -(2-methoxy-5-chlorophenylthio)-desoxybenzoin with benzoin²² also agrees with the same mechanism. When the intermediate corresponding to VII is reached, the reaction proceeds no further, due to steric hindrance.

Acknowledgment.—The authors are indebted to The Research Corporation for a Frederick Gardner Cottrell grant and to Dr. F. C. Nachod of the Sterling-Winthrop Research Institute for determining the infrared absorption spectra.

Experimental²³

Materials.-Commercial samples of 5,5-dimethyl-1,3cyclohexanedione, acetophenone, propiophenone, ethyl benzoylacetate and thiophenol were used without further purification. 2-Methyl-1-indanone and 2-methyl-1-tetralone were prepared by T. Bowen and R. D. Moss in this Laboratory. Benzyl mercaptan was prepared from benzyl chloride via the isothiuronium salt according to known procedures. 24,85 Isobutyrophenone and desoxybenzoin²⁶ were synthesized by a Friedel-Crafts reaction with the corresponding acid chlo-rides.²⁷ Pivalophenone resulted from the alkylation of iso-butyrophenone with methyl iodide.²⁸ Ethyl β -phenylthio-cinnamate was prepared in a 9.4% yield by the addition of thiophenol to ethyl phenylpropiolate according to the pro-cedure of Ruhemann and Stapleton.¹⁶ Hydrolysis of ethyl β-phenylthiocinnamate in ethanolic potassium hydroxide¹⁵

(22) W. A. Mitchell and S. Smiles, J. Chem. Soc., 1529 (1933).

(23) Melting points and boiling points are uncorrected.
(24) A. I. Vogel, "A Textbook of Practical Organic Chemistry,"

Longmans Green and Co., London, 1948, p. 840.

(25) A. J. Speziale, Org. Syntheses, **30**, 35 (1950).
(26) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and (27) The over-all yields were found to be greatly improved by

using the crude acid chlorides, made with thionyl chloride, instead of isolating and purifying them prior to the acylation step.

(28) A. Haller and E. Bauer, Comptonend., 148, 70 (1909),

alcohol. Recrystallization from methanol yielded 6 g. of benzyl 2-methyl-3-indenyl sulfide, which melted at 73-74°.

Anal. Caled. for C₁₇H₁₆S: S, 12.68. Found: S, 12.45. Oxidation of Benzyl 2-Methyl-3-indenyl Sulfide .-- Oxidation of 0.5 g. of uncrystallized benzyl 2-methyl-3-indenyl sulfide with 1.2 ml. of 30% hydrogen peroxide according (20%) of benzyl 2-methyl-3-indenyl sulfone, m.p. 135–137°, which after recrystallization from methanol melted at 138-139°.

Anal. Calcd. for C17H16O2S: S, 11.27. Found: S, 11.14.

5,5-Dimethyl-3-phenylthio-2-cyclohexenone.—A mixture consisting of 7 g. (0.05 mole) of 5,5-dimethyl-1,3-cyclohexanedione and 11 g. (0.1 mole) of thiophenol in 75 ml. of absolute ethyl alcohol was saturated with anhydrous hydrogen chloride. After standing at room temperature for 36 hours, the reaction mixture was taken up in ether and washed sucthe reaction mixture was taken up in ether and washed successively with water, aqueous sodium carbonate and water. Upon evaporation of the dried ether solution, a viscous yel-low oil remained which deposited 3 g. (26%) of pale yellow crystals, m.p. $45-50^{\circ}$, which after recrystallization from methanol gave 2 g. (17%) of 5,5-dimethyl-3-phenylthio-2-cyclohexenone, m.p. $50-51^{\circ}$.

Anal. Calcd. for C14H16OS: S, 13.79. Found: S, 14.02. Acetophenone Diphenyl Mercaptal (IIa) .- A current of hydrogen chloride was passed into a mixture of 6 g. (0.05 mole) of acetophenone and 11 g. (0.1 mole) of thiophenol until the mixture froze to a mass of crystals weighing 14.5 g. and melting at $45-51^{\circ}$. Recrystallization from ethyl alcohol yielded 13.5 g. (84%) of acetophenone diphenyl mercaptal, m.p. $54.5-55^{\circ}$.

Anal. Caled. for C₂₀H₁₆S₂: S, 19.87. Found: S, 20.07. The compound was unstable to moisture, readily decom-

posing in air, but a sample store to most inc, feading desiccator over calcium sulfate remained crystalline for three months. Phenyl 1-Phenyl-1-propenyl Sulfide (IIIc).—A mixture of 6.7 g. (0.05 mole) of propiophenone and 11 g. of thio-phenol was saturated with hydrogen chloride and allowed to ottand at room temperature convict. The following dow stand at room temperature overnight. The following day, the reaction mixture was taken up in ether and the ether solution washed successively with water, aqueous sodium carbonate and water. Upon evaporation of the dried ether extract, 9.5 g. (84%) of a brown viscous oil remained. Dis-tillation of the oil yielded a light yellow oil, b.p. 121-125%at 0.8 mm., which finally solidified after refrigeration and trituration with cold methanol. Recrystallization from methanol gave colorless crystal of phenyl 1-phenyl-1-pro-penyl sulfide, m.p. 42-42.5°.

Anal. Caled. for C₁₅H₁₄S: S, 14.16. Found: S, 13.97.

(29) A. Pomerantz and R. Connor, THIS JOURNAL, 61, 3386 (1939).

^{(21) (}a) T. Posner, Ber., 35, 506 (1902); (b) M. Romero and J. Romo, Bol. Inst. Quim. (Mex.), IV, 3 (1952).

The crystalline material readily decomposes to a light yellow oil at room temperature but remains unchanged in the refrigerator.

Oxidation of Phenyl 1-Phenyl-1-propenyl Sulfide.—Nineteen grams of the brown viscous crude sulfide, oxidized with potassium permanganate according to the method of Bost, Turner and Norton³⁰ furnished mainly benzoic acid and benzenesulfonic acid along with 1.5 g. (7%) of phenyl 1-phenyl-1-propenyl sulfone, m.p. 90–92°.

Anal. Caled. for $C_{15}H_{14}O_2S$: S, 12.41. Found: S, 12.53.

Phenylthiostilbene (IIId).—A solution of 9.8 g. (0.05 mole) of desoxybenzoin and 11 g. of thiophenol in 100 ml. of absolute ethyl alcohol was saturated with hydrogen chloride. After standing 1 hour, the reaction mixture was poured into water, extracted with ether and the ether extract washed successively with water, 2% sodium hydroxide solution and water, dried and distilled. The distillate yielded 1.3 g. of desoxybenzoin and the residue amounted to 11 g. (76%) of a viscous yellow oil which solidified, upon cooling, to a nearly colorless solid, m.p. $35-42^{\circ}$. Recrystalization from methanol gave two fractions: (1) 8 g., m.p. $48-54^{\circ}$, and (2) 2 g., m.p. $50-60^{\circ}$. After repeated fractional recrystallizations from methanol, fraction 1 gave 3.7 g. of phenylthiostilbene, melting at $49-50^{\circ}$.

Anal. Caled. for C₂₀H₁₆S: S, 11.11. Found: S, 10.94.

Repeated fractional recrystallizations of fraction 2 from methanol finally yielded 0.31 g. of an isomer of phenylthiostilbene, m.p. $63-64^{\circ}$.

Anal. Caled. for C₂₀H₁₆S: S, 11.11. Found: S, 11.18. Ethyl β , β -Bis-(phenylthio)-hydrocinnamate (IIb).—A mixture of 19.2 g. (0.1 mole) of ethyl benzoylacetate, 22 g. (0.2 mole) of thiophenol and 20 g. of freshly fused zinc chloride was saturated with hydrogen chloride. After saturation, the reaction flask was tightly stoppered and shaken vigorously for about 10 minutes while the contents gradually solidified. The solid material was dissolved in ether and the ether solution washed successively with water, aqueous sodium carbonate and water. Evaporation of the dried ether solution deposited a light yellow solid which after washing with cold methanol amounted to 15 g. (38%) of colorless crystals, which melted at 87–90°. Recrystallization from methanol yielded 13 g. (33%) of ethyl β , β -bis-(phenylthio)-hydrocinnamate, melting at 92–93°. This melting point was depressed by admixture with ethyl β phenylthocinnamate.

Anal. Calcd. for $C_{23}H_{22}O_2S_2$: S, 16.20. Found: S, 16.16.

Oxidation of Ethyl β , β -Bis-(phenylthio)-hydrocinnamate.—Oxidation of 3.9 g. (0.01 mole) of IIb with 30 ml. of 30% hydrogen peroxide according to the method of Pomerantz and Connor²⁹ yielded mostly benzoic acid along with 0.06 g. (2%) of colorless needles, m.p. 104–105°, which analyzed correctly for ethyl β -phenylsulfinylcinnamate.

Anal. Calcd. for C₁₇H₁₆O₃S: S, 10.68. Found: S, 10.73.

(30) R. W. Bost, J. Turner and R. D. Norton, THIS JOURNAL, 54, 1986 (1932).

Hydrolysis of Ethyl β , β -Bis-(phenylthio)-hydrocinnamate. —Refluxing of a solution of 5.7 g. (0.014 mole) of IIb and 3 g. of potassium hydroxide in 50 ml. of ethyl alcohol for one hour, followed by evaporation of the reaction mixture to dryness furnished a yellow paste which was taken up in a small volume of water and set aside overnight. The next day, a crop of colorless platelets was filtered off and dissolved in water. Acidification of the aqueous solution liberated 1.5 g. (28%) of β -phenylthiocinnamic acid, which after recrystallization from dilute ethanol melted at 192–193° dec.

Anal. Calcd. for C₁₅H₁₂O₂S: S, 12.46. Found: S, 12.35.

When the acid was heated, decomposition, accompanied by gas evolution, occurred with the formation of yellow oil which precipitated acetophenone 2,4-dinitrophenylhydrazone, m.p. 247°,³¹ when treated with acidic 2,4-dinitrophenylhydrazine reagent. The melting point of this acid was depressed by admixture with the β -phenylthiocinnamic acid, m.p. 160–163° dec., obtained by the hydrolysis of ethyl β phenylthiocinnamate.

Phenyl 1-Phenyl-2-methyl-1-propenyl Sulfide (IVe).—A mixture of 14.8 g. (0.1 mole) of isobutyrophenone, 22 g. (0.2 mole) of thiophenol and 25 g. of freshly fused zinc chloride in 20 ml. of absolute ethyl alcohol was saturated with hydrogen chloride, and allowed to stand overnight. Two layers separated in the reaction mixture, the lower one of which contained a solid. From the lower layer, 2 g. of colorless crystals, m.p. $36-37^{\circ}$, were isolated which after several recrystallizations from methanol melted at 38- 38.5° . The identity of this product was not established, but its elemental analysis indicated a composition approximating that required for $C_{28}H_{26-28}S_3$.

Anal. Calcd. for $C_{23}H_{26-23}S_3$: C, 73.33-73.00; H, 5.69-6.13; S, 20.98-20.87. Found: C, 73.29, 73.04; H, 6.17, 6.20; S, 21.19, 21.42.

From the upper layer, 20 g. (83%) of a light yellow oil was obtained which after fractional distillation yielded 15 g. of distillate, boiling at 128–132° at 1 mm. Upon cooling, both the distillate and the residue solidified, and melted at 31–36°. Recrystallization from cold methanol gave 8 g. of phenyl 1-phenyl-2-methyl-1-propenyl sulfide, m.p. 35-36°.

Anal. Calcd. for $C_{16}H_{16}S$: S, 13.34. Found: S, 13.12.

Reaction of Thiophenol with Pivalophenone.—From the reaction of 8.1 g. (0.05 mole) of pivalophenone, 11 g, of thiophenol and 10 g. of freshly fused zinc chloride in 25 ml. of absolute ethyl alcohol, treated in the same manner as described above, 6 g. of starting ketone was recovered along with 1 g. of diphenyl disulfide, m.p. 58–59°.

Anal. Calcd. for C₁₂H₁₀S₂: S, 29.32. Found: S, 29.48.

The melting point of this substance was not depressed by admixture with an authentic sample of diphenyl disulfide, obtained by the air oxidation of thiophenol in ammoniacal ethanol solution.

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(31) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948 p. 263.