the stable cations, whereas the starting state would be analogous to what has been pictured here as the intermediate to exchange between the cations.

Experimental

Materials.—The preparations of 1,2,3,4-tetramethylcyclobutene-1,2-diol dibenzoate and di-*p*-nitrobenzoate have been described previously.[3] The substituted benzoic acids employed were Eastman White Label or samples of comparable purity. Concentrated sulfuric acid (Baker's analyzed, 96–97% H_2SO_4) was used.

Determination of N.m.r. Spectra of Bridged Cations.—The positions of the methyl absorption of the different bridged cations (I and derivatives) were determined by addition of 30–60 mg. of the substituted benzoic acid to a solution (chilled to 0°) of about 50 mg. of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene in 0.4 ml. of concentrated sulfuric acid. After 5–10 mg. of tetramethylammonium fluoborate had been added, the n.m.r. spectrum was determined immediately. In all cases, in addition to the reference signal of the tetramethylammonium ion (τ 6.87) and the peak due to the chloro τ 8.0–8.2 cation II (τ 7.44), a new sharp singlet was observed in the region. Several successive determinations of the n.m.r. spectrum of any particular solution gave an intensification of the new peak and a corresponding decrease in intensity of the peak at τ 7.44. In all cases, these two peaks reached constant relative values in less than 30 min.

Determination of Exchange Equilibrium Constants.—In a manner similar to the above procedure there was added to solutions (at room temperature) of 40–70 mg. of the diesters in 0.4 ml. of concentrated sulfuric acid 30–70 mg. of a substituted benzoic acid and a few milligrams of tetramethylammonium fluoborate. The mixtures were shaken until they were homogeneous and then their n.m.r. spectra were determined immediately followed by additional spectral determinations at 5 to 10 min. intervals. In each case, an additional peak appeared after a few minutes and intensified as the peak due to the cation from the original diester decreased in intensity. The peaks reached constant relative intensities within 2 hr. and no further changes were noted after 24 hr. at room temperature.

Calculation of Exchange Equilibrium Constants.—Calculation of each exchange equilibrium constant required the knowledge of the relative concentration of the four species shown in eq. 1 and 2. In the case of equilibria established by adding a monosubstituted benzoic acid to the dibenzoate ester to give benzoate cation A, protonated substituted benzoic acid B, substituted cation C, and protonated benzoic acid D, four sufficient and independent relations are the following.

$$5A + 4B + 4C + 5D = \text{low-field area (in arbitrary units)}$$

$$12A + 12C = \text{high-field area (in arbitrary units)}$$

$A + 2C - D = 0$ (condition that equates benzoate fragments to twice the cyclobutyl fragments)

$RA - C = 0$ (condition that peak heights of the high-field absorptions are in the ratio of $R{:}1$ = substituted benzoate cation–benzoate cation)

When these equations are solved simultaneously, the expression for K_x in terms of the relative total low-field to total high-field areas and the ratio, R, between the pair of high field peaks is

$$K_x = \frac{4R^2 + 2R}{(6R + 6)(\text{low-field area–high-field area}) - 7R - 5}$$

In the special case where $R = 1$, this expression reduces to the much simpler expression.

$$K_x(R = 1) = \frac{1}{\text{low-field area–high field area}) - 2}$$

In the second case of equilibria established by adding benzoic acid to a nitro-substituted ester, the third condition changes to

$2A - B + C = 0$ (substituted benzoate fragments are equal to twice the cyclobutyl fragments)

and the expression for K_x becomes

$$K_x = \frac{(\text{low-field area–high-field area})(12R^2 + 12R) - 8R^2 - 13R}{5R + 10}$$

where R is the ratio of nitrobenzoate cation–benzoate cation.

In the third case of equilibria established by adding X-substituted benzoic acid to a nitro-substituted ester, conditions one and three differ from those of the first case.

$$4A + 4B + 4C + 4D = \text{low-field area}$$
$$2A - B + C = 0$$

and the expression for K_x becomes

$$K_x = \frac{[\text{nitro cation}][\text{protonated added acid}]}{[\text{cation from added acid}][\text{protonated nitrobenzoic acid}]} = \frac{(\text{low-field area–high-field area})(3R^2 + 3R) - 2R^2 - 3R}{R + 2}$$

where R is the ratio of nitrobenzoate cation–X-substituted benzoate cation.

In all three cases the first two conditions involving low-field and total high-field areas can be replaced by either the pair of weight conditions a and b or the pair b and c.

(a) $A + C$ = relative amount (in moles) of ester added
(b) $B + C$ = relative amount (in moles) of acid added
(c) $A + D$ = two times the relative amount (in moles) of ester added

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Chemistry of Aliphatic Disulfides. VIII. Alkoxide Cleavage of 1,6-Diphenyl-3,4-dithia-1,6-hexanedione (Diphenacyl Disulfide)[1,2]

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The previously reported conversion of 1,6-diphenyl-2,3-dithia-1,6-hexanedione (diphenacyl disulfide, I) to 1,4-diphenyl-1,4-butanedione (V) with 1 equiv. of ethoxide ion has been confirmed. In addition a 1,2,4,5-tetrathiane salt (XI) and acetophenone are obtained. Treatment of I with 2 equiv. of ethoxide provides dipotassio 1,4-diphenyl-1,4-butanedione-2,3-dimercaptide (XXVIII). With 0.25 to 0.1 equiv. of ethoxide 1,5-diphenyl-3-thiapentane-1,5-dione (XXIV) resulted.

Reactions involving nucleophilic attack on a bivalent sulfur atom have received considerable attention during the last 30 years. Within this general area, fission of disulfides with alkaline reagents has attracted con-

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[1] Supported in part by a Frederick Gardner Cottrell Grant from the Research Corporation and by Research Grant RG-7966 from the National Institute of General Medical Sciences of the National Institutes of Health, U. S. Public Health Service.

[2] Part VII of this series: R. G. Hiskey and D. N. Harpp, *J. Am. Chem. Soc.*, **86**, 2014 (1964).

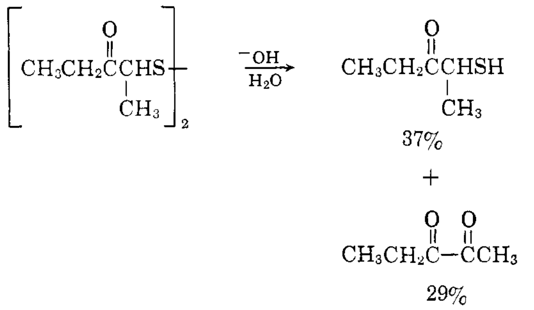
[3] Union Carbide Chemical Corp. Fellow, 1959–1960.

[4] Abstracted in part from dissertations submitted to the University of North Carolina in partial fulfillment of the requirements for the Ph.D. degree, by B. D. Thomas, June, 1962, and J. A. Kepler, Aug., 1963.

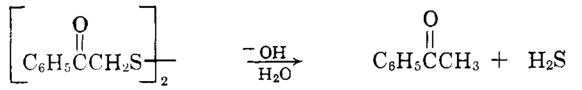
[5] Shell Chemical Corp. Fellow, 1962–1963.

tinuing interest. In general, four mechanistic pathways of alkaline disulfide cleavage have evolved from these studies.[6] The mechanistic proposals account for the observed formation of olefins, mercaptans, sulfides, dithiohemimercaptals, and either thiocarbonyl or carbonyl compounds from various disulfides.

A. Direct displacement of a mercaptide by nucleophilic attack of hydroxide ion on a disulfide sulfur atom was first suggested by Schoberl, *et al.*[7] Although positive evidence for the other proposed primary cleavage product, the alkylsulfenic acid, is lacking, the "direct displacement" mechanism has been invoked in a number of circumstances. For example, Asinger, *et al.*,[8] explained the products obtained from the hydroxide cleavage of several β',β'-diketo disulfides in this manner. Although the "direct displacement" mechanism has been questioned,[9] cyanide ion cleavage of the sulfur–sulfur bond has been clearly shown to proceed by this mechanism; however, since cyanide ion is considered to be more "S-nucleophilic" than hydroxide ion,[6c] the two reactions may not be comparable.



$$\left[CH_3CH_2\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}}HS-\right]_2 \xrightarrow[H_2O]{^-OH} CH_3CH_2\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}}HSH \; (37\%) + CH_3CH_2\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_3 \; (29\%)$$

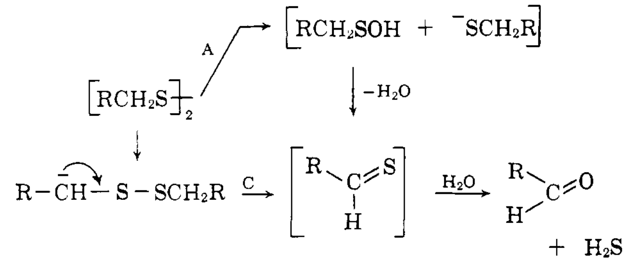


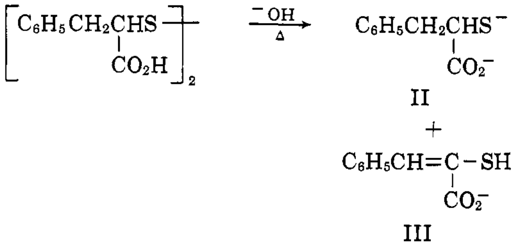
$$\left[C_6H_5\overset{O}{\overset{\|}{C}}CH_2S-\right]_2 \xrightarrow[H_2O]{^-OH} C_6H_5\overset{O}{\overset{\|}{C}}CH_3 + H_2S$$

I

B. β-Elimination of a mercaptide was also proposed[6a] as a possible decomposition pathway of certain disulfides. Swan[10a] suggested that the cystine to lanthionine conversion followed this route and later showed[10b] that α,α'-dimethylcystine was unaffected by basic conditions in which cystine decomposed. More recently, Wallace,[11] *et al.*, reported several additional examples of disulfide decomposition by β-elimination. Danehy and Kreuz[12] have commented on transformations of this general type and have pointed out that no aliphatic disulfide other than protein-bound cystine has been preparatively converted to a sulfide with alkali.

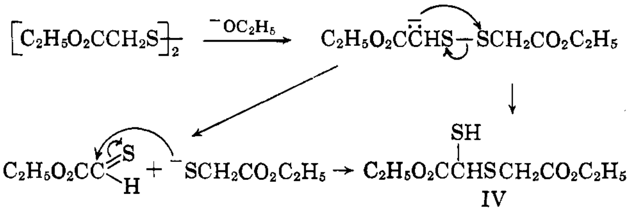
C. α-Elimination of a mercaptide was proposed as the alternative mechanism to the "direct displacement" pathway.[9] Since the two mechanisms could ultimately provide the same products, considerable controversy has surrounded these two possibilities. Although thio aldehydes have not been isolated from the alkaline decomposition of disulfides, thio ketones have been obtained. For example hydrolysis of diphenyldithiadilactic acid provided the mercaptide II and α-mercaptocinnamic acid (III).[13] Normally thiocarbonyl compounds are hydrolyzed to hydrogen sulfide and a carbonyl compound in aqueous alkali.[12]





$$\left[C_6H_5CH_2\underset{CO_2H}{\underset{|}{C}}HS-\right]_2 \xrightarrow[\Delta]{^-OH} \underset{\text{II}}{C_6H_5CH_2\underset{CO_2^-}{\underset{|}{C}}HS^-} + \underset{\text{III}}{C_6H_5CH=\underset{CO_2^-}{\underset{|}{C}}-SH}$$

D. Intramolecular decomposition, following removal of an α-hydrogen atom, has recently been proposed by Howard.[14] This suggestion was based on the observation that treatment of diethyl dithiadiglycolate with ethoxide ion at −50° provided diethyl 2-mercapto-3-thiaglutarate (IV). These results could also be explained by assuming initial α-elimination of mercaptide followed by nucleophilic addition of the mercaptide to the thiocarbonyl group.



IV

Groth[15] reported a transformation which appears to be unique among the reactions of disulfides. When 1,6-diphenyl-2,3-dithia-1,6-hexanedione (diphenacyl disulfide, I) was allowed to stand with 1 equiv. of potassium ethoxide in ethanol for 14 days, a 39% yield of 1,4-diphenyl-1,4-butanedione (V) resulted. Although

$$\underset{\text{I}}{[C_6H_5COCH_2S]_2} \xrightarrow[C_2H_5OH]{KOC_2H_5} \underset{\text{V}}{C_6H_5COCH_2CH_2COC_6H_5}$$

Groth reported several additional reactions of I and of 2-mercaptoacetophenone (phenacyl mercaptan, VI),[16]

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(6) A number of reviews of this aspect of sulfur chemistry have appeared. These include (a) D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 11 (1951); (b) A. Schoberl and A. Wagner, Houben-Weyl, "Methoden der organischen Chemie," Vol. 9, E. Müller, Ed., 4th Ed., Georg Thieme, Stuttgart, 1955; Vol. 11 (2), 1958; (c) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959); (d) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1960, p. 362; (e) O. Foss, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, London, 1961.

(7) A. Schoberl, *Ann.*, **507**, 111 (1933); A. Schoberl, E. Berninger, and F. Harren, *Ber.*, **72B**, 1545 (1934).

(8) F. Asinger, M. Thiel, and W. Schafer. *Ann.*, **637**, 146 (1960).

(9) N. A. Rosenthal and G. Oster, *J. Soc. Cosmetic Chemists*, **5**, 286 (1954).

(10) (a) J. M. Swan, *Angew. Chem.*, **68**, 215 (1956); (b) I. W. Stapleton and J. M. Swan, *Australian J. Chem.*, **13**, 416 (1959).

(11) T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 2739 (1963).

(12) J. P. Danehy and J. A. Kreuz, *ibid.*, **83**, 1109 (1961).

(13) A. Schoberl and H. Eck, *Ann.*, **523**, 97 (1936).

(14) E. G. Howard, *J. Org. Chem.*, **27**, 2212 (1962).

(15) B. Groth, *Arkiv Kemi Mineral. Geol.*, **9**, 1 (1924).

(16) B. Groth, Dissertation, Uppsala, 1926.

no further clarification of this conversion was accomplished. The present investigation concerns a more detailed study of the ethoxide cleavage reactions of I; the accompanying papers cover the reactions of some unsymmetrical analogs of I[17] and evidence supporting the proposed mechanism for the conversion of I to V.[18] The numerical designations of compounds given in this paper are used in the subsequent papers.

Ethoxide Cleavages of I. A. 1:1 Base to Disulfide Ratio.—When I, prepared by either procedure of Price and Twiss,[19] was treated with 1 equiv. of potassium ethoxide in ethanol, 39% of V, acetophenone, and hydrogen sulfide were obtained. The authenticity of V was demonstrated by a comparison with an authentic sample and by conversion to 2,5-diphenylfuran. In a similar manner 1,4-di-*p*-bromophenyl-3,4-dithia-1,6-hexanedione (VII) was converted to 1,4-di-*p*-bromophenyl-1,4-butanedione (VIII) in 38% yield. A 15% yield of *p*-bromoacetophenone (IX) was also obtained. Subsequently it was established that similar yields of V or VIII could be obtained after 72 hr. at room temperature.

$$\underset{\text{VII}}{[p\text{-BrC}_6\text{H}_4\text{COCH}_2\text{S}]_2} \longrightarrow \underset{\text{VIII}}{[p\text{-BrC}_6\text{H}_4\text{COCH}_2\text{—}]_2} + \underset{\text{IX}}{p\text{-BrC}_6\text{H}_4\text{COCH}_3}$$

The effects of temperature, oxygen, and the nature of the base employed on the yield of V from I were initially studied. The results of these experiments are summarized in Table I. Of interest in these experiments was the fact that V resulted from I using sodamide in dry ether or ether containing a trace of methanol. Thus an initial acid–base reaction rather than a nucleophilic attack by base was suggested. When the ethoxide consumption in the reaction was followed by titration, the ethoxide concentration was not altered until the precipitated V was removed.

TABLE I

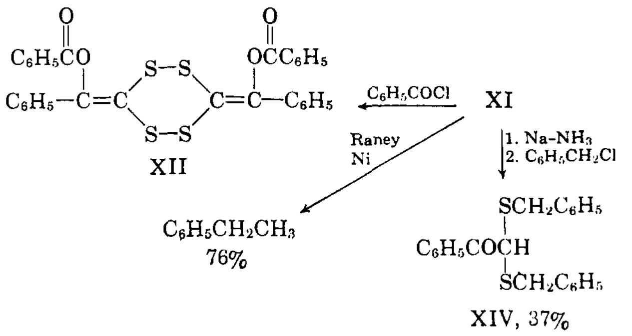
ALKALINE CLEAVAGES OF DIPHENACYL DISULFIDE[a]

Catalyst[b]	Temp., °C.	% yield of V
$C_2H_5O^-$	25	35–39
$C_2H_5O^-$[c]	25	34
$C_2H_5O^-$[d]	0	9–12
$C_2H_5O^-$	78	23
LiOH[e]	25	30
$NaNH_2$[f]	25	35
$NaNH_2$[g]	25	34
$t\text{-}C_4H_9O^-$	78	31

[a] Cleavages were conducted in dry ethanol for 72 hr. unless otherwise noted. [b] A base to disulfide ratio of 1:1 was employed. [c] Oxygen was excluded. [d] Filtration of the precipitated V provided a clear solution which afforded an additional 22% of V after 72 hr. at 25°. [e] In dilute ethanol. [f] In dry ether. [g] In dry ether containing a trace of methanol.

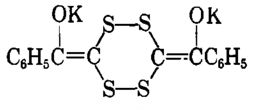
Cleavage of I with 1 equiv. of ethoxide in ethanol invariably provided sizable quantities of a polymeric yellow solid which could not be purified. The infrared spectrum of the material was similar to that of I and V. Desulfurization of the yellow solid with Raney nickel gave a 30% yield of either 1,4-diphenylbutane (X) or V, depending on the conditions employed, together with some acetophenone. Thin layer chromatography of an acetone extract of the yellow solid indicated the presence of I and V in addition to several unidentified spots. Sulfur could also be isolated from the acetone extract. The nature of the polymeric yellow solid is presently not known.

Structure of XI.—When the solution remaining after removal of the precipitated V was acidified with carbon dioxide rather than sulfuric acid, a yellow dipotassio salt (XI) was obtained in 17% yield. The substance exhibited absorption in the infrared characteristic of olefinic unsaturation. The ultraviolet spectrum showed maxima at 323 mμ (ε 28,000) and 230 mμ (ε 24,600). The material failed to give qualitative tests for sulfhydryl and enol. Desulfurization of the salt with Raney nickel provided ethylbenzene in 76% yield.

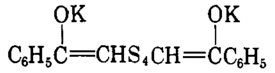


Treatment of XI with benzoyl chloride in ether provided the dibenzoate derivative XII. The dibenzoate exhibited a single carbonyl peak at 1735 cm.$^{-1}$ and a ultraviolet maximum at 276 mμ (ε 23,500).

These data were compatible with two possible formulations for the salt, the 1,2,4,5-tetrathiane XI or the linear tetrasulfide XIII. The stability of the material



XI



$$\mathrm{C_6H_5\overset{OK}{C}{=}CHS_4CH{=}\overset{OK}{C}C_6H_5}$$

XIII

to base, the low pK_a, and the presence of only aromatic protons in the n.m.r. spectrum favored the former possibility.

More conclusive evidence favoring XI was obtained by sodium in liquid ammonia reduction of the salt. The resulting mercaptide was alkylated directly with benzyl chloride to provide the dithioacetal XIV in 37% yield. Although the infrared spectrum of XIV was similar to that of 1,4-diphenyl-3-thiabutanone (XV) a mixture melting point with XV was depressed. The n.m.r. spectrum of XIV provided confirmatory evidence for the dithioacetal structure and thus the 1,2,4,5-tetrathiane structure XI. The spectrum of XIV (Table II) appeared as a pair of doublets exhibiting AB-type splitting and was similar to the spectrum of dibenzyl dithiabenzal (XVI). The AB splitting observed in XIV and XVI was not observed in the spectrum of dibenzthial (XVII). The nonequivalence of the benzyl protons in XIV and XVI is not unexpected; Coyle and Stone[20] have reported that the borohydride complex of diethyl sulfide (XVIII)

$$\underset{\text{XV}}{\mathrm{C_6H_5COCH_2SCH_2C_6H_5}} \quad \underset{\text{XVI}}{\mathrm{C_6H_5CH(SCH_2C_6H_5)_2}} \quad \underset{\text{XVII}}{\mathrm{CH_2(SCH_2C_6H_5)_2}}$$

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[17] R. G. Hiskey and J. A. Kepler, *J. Org. Chem.*, **29**, 3678 (1964).

[18] R. G. Hiskey, J. A. Kepler, and B. D. Thomas, *ibid.*, **29**, 3684 (1964).

[19] T. S. Price and F. T. Twiss, *J. Chem. Soc.*, **95**, 1489 (1909); F. T. Twiss, *ibid.*, **105**, 36 (1914).

[20] T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961).

TABLE II
N.M.R. DATA[a]

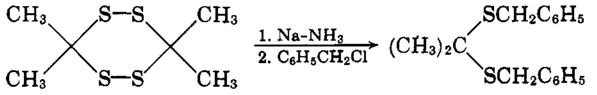
Compd.	τ	Integration	Multiplicity[b]
	6.35	2	d (J = 13.5 c.p.s.)
XIV	6.07	2	d (J = 13 c.p.s.)
	5.14	1	s
	2–3	15.6	m
XVI	6.63	2	d (J = 14 c.p.s.)
	6.33	2	d (J = 13 c.p.s.)
	5.66	1	s
	2–3	15.2	m
XVII	6.77	1	s
	6.26	2	s
	2–3	5	m
XXVIb	7.71	2.96	s
	4.02	1	s
	2–3	5	m

[a] Spectra were recorded with a Varian A-60 spectrometer in deuteriochloroform containing tetramethylsilane as internal standard. [b] s, singlet; d, doublet; m, aromatic multiplet.

exhibits two overlapping quartets for the methylene protons. Waugh and Cotton[21] observed a similar coupling phenomenon in the spectrum of diethyl acetal (XIX); the coupling is absent in ethylal (XX).

$$\underset{\text{XVIII}}{(CH_3CH_2)_2SBH_3} \qquad \underset{\text{XIX}}{CH_3CH(OCH_2CH_3)_2} \qquad \underset{\text{XX}}{CH_2(OCH_2CH_3)_2}$$

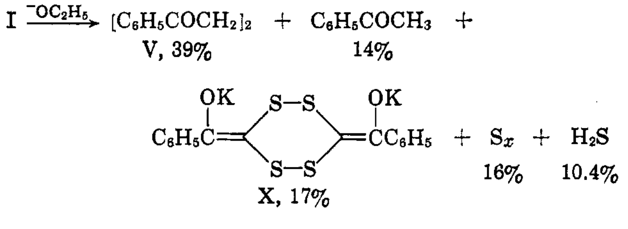
The conversion of XI to XIV is similar to the transformation of XXI to XXII reported by Magnusson.[22]



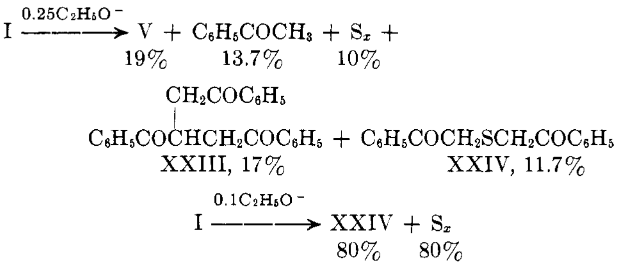
XXI XXII

A complete determination of the products obtained from the action of 1 equiv. of ethoxide ion on I gave the results indicated in Scheme I.

SCHEME I



B. Base to Disulfide Ratios Less than 1:1.—Although the products resulting from the action of 1 equiv. of ethoxide on I were the same under a variety of conditions, somewhat different results were obtained when the base to disulfide ratio was varied. Treatment of I with 0.5 equiv. of ethoxide provided 7% of 1,2,3-tribenzoylpropane (XXIII), besides the products previously isolated (Table III). When I was allowed to stand with 0.25 equiv. of ethoxide, an 11.7% yield of 1,5-diphenyl-3-thiapentane-1,5-dione (XXIV) was also produced. In one experiment when the base to disulfide ratio was lowered to 0.1, I afforded only XXIV and sulfur. Both products were obtained in 80% yield.

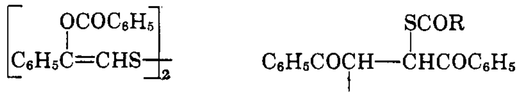


$$\mathrm{I} \xrightarrow{0.25C_2H_5O^-} \underset{19\%}{\mathrm{V}} + \underset{13.7\%}{C_6H_5COCH_3} + \underset{10\%}{S_x} +$$

$$\underset{\text{XXIII, 17\%}}{C_6H_5CO\overset{CH_2COC_6H_5}{CH}CH_2COC_6H_5} + \underset{\text{XXIV, 11.7\%}}{C_6H_5COCH_2SCH_2COC_6H_5}$$

$$\mathrm{I} \xrightarrow{0.1C_2H_5O^-} \underset{80\%}{\mathrm{XXIV}} + \underset{80\%}{S_x}$$

C. 2:1 Base to Disulfide Ratio. XXVIII Structure.—Treatment of I with 2 equiv. of ethoxide led to a completely different product. Groth[15] reported that the direct addition of 2 equiv. of potassium ethoxide to I yielded a salt (XXVIII) which crystallized from the reaction mixture. Groth converted the salt to a dibenzoate, assigned as XXV, which melted at 168–169°. His assignment of structure XXV was made on the basis of the elemental analysis and molecular weight of the substance. When Groth's experiment was repeated in our laboratory, the salt XXVIII and the 168–169° dibenzoate were obtained. However, when I was allowed to dissolve in a solution containing 1 equiv. of ethoxide and then treated with a second equivalent of ethoxide, the precipitated salt led to a dibenzoate derivative XXVIa, which melted at 190–192°. The dibenzoate XXVIa gave a negative sodium nitroprusside test for mercaptan or disulfide, whereas XXVIII, the salt from which it was derived, gave a positive test for mercaptan. The infrared spectrum of XXVIa exhibited absorption peaks at 1675 and 909 cm.$^{-1}$, similar to those present in phenacyl thiobenzoate (XXVII). Positive evidence for the structure of XXVIa was obtained by desulfurization of the substance. Treatment of XXVIa with Raney nickel in refluxing ethanol provided V in 66% yield.



XXV

XXVIa, R = C_6H_5
b, R = CH_3

$$\mathrm{XXVIa} \xrightarrow{\text{Raney Ni}} \underset{\text{V, 66\%}}{C_6H_5COCH_2CH_2COC_6H_5} + C_6H_5CH_2OH$$

Analysis of the reaction mixture in the vapor fractometer, after removal of V, indicated benzyl alcohol was the only volatile component.

Initially it was assumed that difference in the mode of addition of ethoxide to I had provided two structurally different dibenzoates, XXV and XXVIa. However, the infrared spectra of the two salts (from the two different modes of addition of ethoxide to I) were identical. On the other hand the infrared spectra of the two dibenzoates (168 and 190°) were quite similar but not identical. In order to settle the matter of identity, the salt obtained by Groth's procedure was benzoylated using the procedure which gave the 190° dibenzoate (XXVIa). The resulting dibenzoate melted at 191–192° and was identical in all respects with XXVIa. Thus the 168° dibenzoate, obtained originally by Groth, is probably a stereoisomer of XXVIa.

Additional support for the 1,2-dimercaptide character of the salt XXVIII was obtained by acylation of the salt. The infrared spectrum of the diacetate XXVIb

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[21] J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

[22] B. Magnusson, *Acta Chem. Scand.*, **16**, 772 (1961).

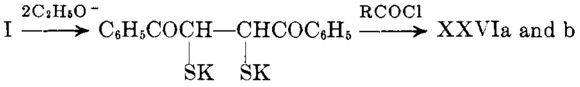
TABLE III

CLEAVAGE PRODUCTS OF I WITH VARIOUS BASE TO DISULFIDE RATIOS

Expt.[a] no.	Molar ratio base–DS	Yield, %							
		V	$C_6H_5COCH_3$	XI	S	H_2S	XXIII	XXIV	XXVIII
A	2	0	0		0	0			85
B	1	39	14	17	16	10.4			
C	0.5	17	17	17	15	*b*	7		
D	0.25	19	13.7		10	*b*	17	11.7	
E	0.1	0	<3		80			80	

[a] Cleavage reactions were conducted in ethanol using potassium ethoxide. The reaction mixtures were allowed to stand at room temperature for 72 hr. [b] Present but not determined quantitatively.

exhibited a conjugated carbonyl peak at 1700 cm.$^{-1}$ and thiol acetate carbonyl absorption at 1668 cm.$^{-1}$. No peak which could be attributed to an enol acetate carbonyl was observed. Therefore, the salt is assigned as dipotassio-1,4-diphenyl-1,4-butanedione-2,3-dimercaptide (XXVIII). The n.m.r. spectrum of XXVIb (Table III) is in agreement with this formulation.



$$\mathrm{I} \xrightarrow{2C_2H_5O^-} \underset{\mathrm{SK}}{\mathrm{C_6H_5COCH}}—\underset{\mathrm{SK}}{\mathrm{CHCOC_6H_5}} \xrightarrow{RCOCl} \mathrm{XXVIa\ and\ b}$$

XXVIII, 85%

In an attempt to independently synthesize XXVIb, 1,2-dibenzoylacetylene (XXIX) was treated with thiolacetic acid and benzoyl peroxide. A low yield of a material analyzing correctly for XXVIb was obtained. The infrared spectra of the two compounds were almost identical; however, the synthetic substance melted from 174–180°, whereas pure XXVIb melted at 202–204°. The n.m.r. spectra of both samples were identical and it was concluded that the synthetic material was probably a mixture of diastereoisomers of structure XXVIb.

The product analysis data from the cleavage of I at various base concentrations is presented in Table III. In experiments B, C, and D the rate of appearance of acetophenone was followed by analysis of acidified aliquots from the reaction mixture in the vapor fractometer. In all cases, the acetophenone concentration increased gradually for the first 20 hr. and became constant. As noted, the final concentrations of acetophenone did not vary significantly over a fourfold change in base concentration. However, in experiment E, a tenfold change in base concentration, less than 3% of acetophenone was produced.

When the sulfide XXIV was allowed to react with 1 equiv. of ethoxide ion under the usual cleavage conditions, no trace of V could be detected. The sulfide was, however, decomposed under these conditions and provided a polymeric yellow solid similar to that obtained from the action of ethoxide on I. Since V could not be detected, the sulfide XIV is assumed not to be an intermediate in the formation of V from I.

Experimental[23,24]

Preparation of 1,6-Diphenyl-3,4-dithia-1,6-hexanedione (I).—Following the procedure of Twiss[19] a solution of 127 g. (0.51 mole) of sodium thiosulfate pentahydrate and 100 g. (0.50 mole) of ω-bromoacetophenone in 500 ml. of 50% ethanol was refluxed for 1 hr. The reaction mixture was concentrated to 50 ml. and the solid was redissolved in 300 ml. of water. The solution was treated with 85 ml. (0.75 mole) of 30% hydrogen peroxide in 100 ml. of 6 *N* sulfuric acid. The oxidation was conducted at 25° over a period of 8 hr. The disulfide was recrystallized from a methylene chloride–ether mixture to give 42 g. (55%) of I, m.p. 79–81°, lit.[15] m.p. 81°.

Anal. Calcd. for $C_{16}H_{14}O_2S_2$: C, 63.64; H, 4.66; S, 21.21. Found: C, 63.41; H, 4.50; S, 21.42.

The ultraviolet spectrum of I in absolute ethanol exhibited a maximum at 246 mμ (ε 24,900). The disulfide could also be prepared in 50% ethanol using iodine as the oxidizing agent.[19] The yield of I by this method was 61% on a smaller scale.

Preparation of 1,6-Di-*p*-bromophenyl-3,4-dithia-5,6-hexanedione (VII).—Prepared according to the procedure of Price and Twiss[19] using iodine as the oxidizing agent. The disulfide was recrystallized from chloroform and was obtained in 75% yield, m.p. 137–138°.

Anal. Calcd. for $C_{16}H_{12}Br_2O_2S_2$: C, 41.75; H, 2.63; S, 13.93. Found: C, 41.52; H, 2.91; S, 13.74.

Preparation of 1,5-Diphenyl-3-thia-1,5-pentanedione (XXIV).—Prepared according to the procedure of Shotte[25] in 63% yield, the product melted at 76–77°, lit.[15] m.p. 77°.

Preparation of 1,2,3-Tribenzoylpropane (XXIII).—The ketone was prepared according to the procedure of Lutz, *et al.*,[26] in 4% yield, m.p. 122–123°, lit.[26] m.p. 122°.

Preparation of 1,4-Diphenyl-3-thiabutanone (XV).—To 2.0 g. (0.01 mole) of phenacyl bromide in a mixture of 5 ml. of dimethyl sulfoxide and 35 ml. of methanol was added 1.24 g. (0.01 mole) of benzyl mercaptan. The solution was refluxed for 10 min., treated with 2 ml. of piperidine, and poured on ice. Recrystallization of the residue from ether provided needles, m.p. 87°, lit.[27] m.p. 87°.

Dibenzyl Dithiabenzal (XVI) and Dibenzthial (XVII) were prepared according to the procedures of Fromm, *et al.*[28a,b]

1,4-Diphenyl-1,4-butanedione (V) was prepared by the procedure of Lutz, *et al.*,[29] m.p. 144–145°, $\lambda_{\max}^{\mathrm{alc}}$ 243 mμ (ε 28,200).

Cleavage of 1,6-Diphenyl-3,4-dithia-1,6-hexanedione (I) with Potassium Ethoxide.—To a solution of 3.28 g. (0.039 mole) of potassium ethoxide in 20 ml. of ethanol was added 10.5 g. (0.035 mole) of I. The disulfide required about 10–15 min. to dissolve. The solution was allowed to stand at 27° for 14 days (in subsequent experiments, 72 hr. unless otherwise noted). The precipitated solid was filtered and washed with dry ethanol to afford 4.2 g. of crude 1,4-diphenyl-1,4-butanedione (V), m.p. 137–146°.

The crude product was washed with water and dried to yield 3.0 g. (36%) of V, m.p. 143–146°. Recrystallization from ethanol raised the melting point to 145–146°. A mixture melting point with an authentic sample occurred at 145–146°.

The filtrate from the reaction mixture was concentrated and the residual red oil partitioned between ether and water. The layers were separated, the water was extracted several times with ether, and the extracts were combined and dried. Removal of the ether *in vacuo* provided an additional 0.2 g. (3%) of V and 1.5 g. of an oil whose infrared spectrum was virtually identical with that of acetophenone.

The aqueous layer was acidified with dilute sulfuric acid and the evolved hydrogen sulfide trapped a lead sulfide (1.45 g., 0.195 g. of sulfur). The acidified water solution was filtered to give 4.77 g. of a polymeric yellow solid which had no sharp melting point

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(23) Melting points and boiling points are uncorrected.

(24) Elemental analyses were performed by Spang Microanalytical Laboratory, Plymouth, Mich., Schwartzkopf Microanalytical Laboratory, Woodside, N. Y., and Micro-Tech Laboratories, Skokie, Ill. The molecular weight determinations were made by Alfred Bernhardt, Mülheim (Ruhr), Germany, and Huffmann Micro-Analytical Laboratories, Wheatridge, Colo.

(25) L. Shotte, *Arkiv Kemi*, **5**, 59 (1953).

(26) R. E. Lutz and F. S. Palmer, *J. Am. Chem. Soc.*, **57**, 1947 (1935).

(27) L. M. Long, *ibid.*, **68**, 2159 (1946).

(28) (a) E. Fromm and A. Forster, *Ann.*, **394**, 388 (1912); (b) E. Fromm, A. Forster, and B. Scherschewitzki, *ibid.*, **394**, 343 (1912).

(29) R. E. Lutz, L. Love, Jr., and F. S. Palmer, *J. Am. Chem. Soc.*, **57**, 1953 (1935).

and contained sulfur. To 1.0 g. of the material in ethanol was added two teaspoonfuls of Raney nickel. The mixture was stirred at reflux for 24 hr., filtered, and concentrated. The oily solid was filtered to give 0.285 g. (29%) of V, m.p. 140–144°, and 0.205 g. of an unidentified red oil. Hydrolysis of the nickel sulfide gave 2.0 g. of lead sulfide, which corresponds to 0.268 g. (27%) of sulfur.

The polymeric yellow solid was chromatographed using thin layer chromatography on silica gel G as solid support and chloroform–benzene (3:4) as eluent. Development of the chromatogram with iodine vapor showed five spots, two of which corresponded to I and V. Trituration of the polymeric solid obtained from 0.03 mole of I with acetone provided 0.29 g. (15%) of sulfur. No other tractable products could be isolated from the acetone solution.

Cleavage of 1,6-Di-*p*-bromophenyl-3,4-dithia-1,6-hexanedione (VII) with Potassium Ethoxide.—A solution containing 1.82 g. (0.0216 mole) of potassium ethoxide and 10 g. (0.0216 mole) of VII in 40 ml. of ethanol was shaken mechanically for 72 hr. The solution was filtered to yield 3.16 g. (39%) of 1,4-bromophenyl-1,4-butanedione (VIII), m.p. 183–185°, lit.[30] m.p. 182°. After several days an additional 0.54 g. (6%) crystallized, m.p. 183–185°.

In a similar experiment in which 39% of the diketone was obtained, the filtrate was concentrated and partitioned between ether and water as described previously. Chromatography of the ether layer on an alumina column provided 1.26 g. (15%) of *p*-bromoacetophenone (IX), m.p. 45–48°. Acidification of the aqueous layer provided 2.1 g. of the yellow polymeric solid.

Cleavage of I with Sodamide in Ether and Added Methanol.—A suspension of 9.06 g. (0.03 mole) of I in 150 ml. of dry ether was vigorously stirred under a nitrogen atmosphere at 0°. The suspension was treated with 1.1 g. (0.03 mole) of sodamide, and the reaction was allowed to proceed at 0° until no more ammonia was evolved (about 12 hr.). The suspension was treated with 0.9 ml. of methanol and stirred at room temperature for an additional 36 hr. The reaction mixture was poured on ice and filtered to give 1.8 g. of V, m.p. 140–145°.

The ether layer was washed with 3% sodium hydroxide solutions and dried over magnesium sulfate. Removal of the solvent and chromatography of the resulting oil on neutral alumina, using benzene–petroleum ether (4:1) as the eluent, gave 0.75 g. (total yield, 36%) of V.

The sodium hydroxide washes were combined with the aqueous layer and acidified. The evolved hydrogen sulfide was trapped as lead sulfide, 0.55 g. (3.9%). The remaining gummy solid was dried over phosphorus pentoxide, partially dissolved in ethyl acetate, and filtered to give 0.4 g. of sulfur. The solvent was removed and the oil (0.8 g.) was chromatographed on neutral alumina. The only tractable product was 0.12 g. of sulfur (total yield, 27%).

Cleavage of I with Sodamide in Ether.—The cleavage was carried out as described with the exception that no methanol was added. The yields of products were V, 34.8%; lead sulfide, 5.3%; and sulfur, 25%.

Dipotassio Salt of 2,6-Dibenzoyl-1,2,4,5-tetrathiane (XI).—To a solution of 2.78 g. (0.033 mole) of potassium ethoxide in 20 ml. of ethanol was added 10 g. (0.033 mole) of I. After 72 hr. 2.84 g. (36%) of V, m.p. 143–146°, was isolated. The ethanol was removed *in vacuo* and the red oil was partitioned between ether and water. The ether layer provided acetophenone as previously described.

The water layer was treated with carbon dioxide until no more hydrogen sulfide was evolved. A small amount of solid was filtered and the filtrate (pH 8) was neutralized with carbon dioxide and extracted with chloroform. The water layer was evaporated *in vacuo* and the solid residue was dissolved in 1.5 ml. of ethanol. The salt XI which crystallized, 1.55 g. (18%), melted at 165–170°. Recrystallization from dilute ethanol raised the melting point to 168–171°.

Anal. Calcd. for $C_{16}H_{12}K_2O_2S_4$: C, 43.40; H, 2.73; K, 17.66; S, 28.97. Found: C, 43.38; H, 1.99; K, 17.52; S, 27.81.

A 300-mg. sample of XI was acidified with methanolic hydrochloric acid. The solid was triturated with methanol, filtered, and dissolved in 25 ml. of chloroform. The solution was washed with water and evaporated. The resulting solid melted at 98–140°. Treatment of this material with potassium ethoxide failed to provide XI. A thin layer chromatogram of the acidified product exhibited three spots, none of which were I or V.

The dibenzoate derivative of XI (XII) was prepared from 2.0 g. (0.0045 mole) of XI and 1.27 g. (0.009 mole) of benzoyl chloride in 50 ml. of ether and 20 ml. of acetone. Reaction occurred immediately and XII crystallized when stored at 3°. The crude product, m.p. 194–196°, was recrystallized from chloroform–acetone to give 1.4 g. of XII, m.p. 204–206°.

Anal. Calcd. for $C_{30}H_{20}O_4S_4$: C, 62.95; H, 3.52; S, 22.38; mol. wt., 573. Found: C, 62.94, 62.85, 61.99; H, 3.48, 3.46, 3.43; S, 20.28, 20.03, 22.36; mol. wt. (Rast), 491, 497, 502, (ebulscopic) 505.

The n.m.r. spectrum of XII showed only aromatic protons.

Desulfurization of XI with Raney Nickel.—To a solution of 0.8 g. (1.8 mmoles) of XI in 20 ml. of ethanol was added 5 teaspoonfuls of Raney nickel in 100 ml. of ethanol. The mixture was stirred under reflux for 20 hr., then filtered through asbestos. About 20 mg. of an oily solid whose infrared spectrum was virtually identical with 1,4-diphenylbutane was collected on the filter.

The filtrate (164.4 g.) gave a negative test with 2,4-dinitrophenylhydrazine. A vapor fractogram of the filtrate was obtained on a Perkin-Elmer Model 154-C vapor fractometer using an 80 cm. × 4 mm. glass column packed with 30–60-mesh Celite containing 5% Carbowax 400. A single peak corresponding to ethyl benzene was present. Trace analysis for ethyl benzene indicated 0.29 g. (76%) (average of two runs: 0.31 and 0.27 g.) was present (*n*-propylbenzene, 52°, helium flow rate 240 cc./min., elution time 150 and 240 sec.).

Reduction of XII with Sodium in Liquid Ammonia.—To 50 ml. of liquid ammonia containing several small pieces of clean sodium was added small portions of XI until the color was discharged. This process was repeated until 1.5 g. (0.0033 mole) of XI had been added. The remaining blue color was then discharged with a small amount of ammonium chloride, stirred 30 min., and the ammonia was allowed to evaporate.

The residue was washed with water, filtered, triturated with ether, and filtered. The remaining solid (0.36 g., m.p. 95–96°) was recrystallized from ether, m.p. 95–96°. Concentration of the filtrate provided an additional 0.4 g. of XIV, m.p. 94–96° (total yield, 37%).

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 72.51; H, 5.52; S, 17.72. Found: C, 71.79, 72.58; H, 5.52, 5.71; S, 17.58.

A mixture melting point with 1,4-diphenyl-2-thiabutanone occurred at 76–81°.

Cleavage of I with Potassium Ethoxide.—To a solution of 1.16 g. (0.0138 mole, 0.5 equiv.) of potassium ethoxide in 30 ml. of ethanol was added 8.35 g. (0.0272 mole) of I. The disulfide slowly dissolved over a 4-hr. period and the solution was stirred for 72 hr. at 28°. Filtration provided 1.54 g. of a mixture of V and sulfur, m.p. 114–144°. The crude product was fractionally crystallized from ethanol to yield 0.82 g. (12.5%) of V, m.p. 142–145°, and 0.24 g. (13.5%) of sulfur, m.p. 114–119°. After 6 days 0.25 g. of crystals was deposited, m.p. 120–143°. The ethanol was removed and the residue was partitioned between ether and water.

The ether layer deposited 0.4 g. of a solid, m.p. 114–143°. Evaporation of the ether solution provided 3.4 g. of a red oil whose only volatile component was acetophenone as indicated from the vapor fractogram. The acetophenone (1.9 g. crude weight, 28%) was removed *in vacuo* and upon addition of ethanol the residue crystallized to yield 0.4 g. of XXIII, m.p. 109–111°. Two recrystallizations from ethanol raised the melting point to 120.5–122.5° (0.25 g., 7%), lit.[26] m.p. 122°. A mixture melting point with an authentic sample was not depressed. The filtrate contained 0.91 g. of a red oil which was not identified.

The aqueous layer was neutralized with carbon dioxide and provided 2.0 g. (17%) of XI, m.p. 165–170°. The dibenzoate derivative XII melted at 200–201°.

Cleavage of I with Potassium Ethoxide.—To a solution of 0.696 g. (0.0083 mole, 0.25 equiv.) of potassium ethoxide in 20 ml. of ethanol was added 10 g. (0.0331 mole) of I. The disulfide was not completely soluble and an additional 20 ml. of ethanol was added. The reaction mixture was shaken 72 hr. at 26°. An oil separated and crystallized on standing to give 1.26 g. of solid, m.p. 77–115°. Recrystallization from ethanol provided 1.05 g. (11.7%) of 1,5-diphenyl-3-thia-1,5-pentanedione (XXIV), m.p. 75–77°, lit.[15] m.p. 77°. A mixture melting point with an authentic sample was not depressed. In addition 0.20 g. of sulfur, m.p. 114–118°, was isolated.

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(30) W. J. Hale and L. Thorp, *J. Am. Chem. Soc.*, **35**, 262 (1913).

The original reaction mixture deposited 1.48 g. (19%) of V, m.p. 139–143°, on standing several days. After several weeks 1.03 g. of solid, m.p. 114–121°, precipitated. Recrystallization from ethanol afforded 0.98 g. (17%) of XXIII, m.p. 119–121°. No attempt was made to obtain any of the salt XI from the aqueous layer.

Cleavage of I with Potassium *t*-Butoxide.—To a solution of 0.143 g. (0.00128 mole, 0.1 equiv.) of potassium *t*-butoxide in 20 ml. of *t*-butyl alcohol was added 4.0 g. (0.0132 mole) of I. The suspension was shaken mechanically for 1 week at room temperature. Filtration afforded 3.2 g. of an oily solid which gave 0.32 g. (81%) of sulfur, m.p. 116–118°, when recrystallized from ethanol. The sulfide XXIV crystallized from the filtrate to give 2.91 g. (81%), m.p. 72–74°. One recrystallization from ethanol raised the melting point to 76–77°. A mixture melting point with an authentic sample of XXIV was not depressed.

Cleavage of I with Potassium Ethoxide. Formation of the Dipotassio Salt of 2,3-Dimercapto-1,4-diphenyl-1,4-butanedione (XXVIII).—Following the procedure of Groth[15] a solution of potassium ethoxide (0.04 mole, 2 equiv.) in 45 ml. of ethanol was treated with 15.2 g. (0.02 mole) of I. The dipotassium salt (XXVIII) crystallized, and the mixture was stored for 18 hr. at 0°. The suspension was then diluted with 50 ml. of ether, allowed to stand for 1 hr., and filtered; the solid was washed with ether. The disalt appeared as orange needles, m.p. 166–170°, 16.0 g. (85%), lit.[15] m.p. 168–170°.

When 10.4 g. (0.0344 mole) of I was treated with 15 ml. of a solution containing 2.61 g. (0.0668 g.-atom) of potassium in 30 ml. of ethanol, the disulfide dissolved. The remaining 15 ml. of ethoxide solution was then added and the solution was kept 72 hr. at room temperature. Filtration of the precipitated salt provided 2.69 g. (21%) of XXVIIII, m.p. 167–170°.

Formation of 2,3-Dibenzoylthio-1,4-diphenyl-1,4-butanedione (XXVIa, R = C_6H_5). A. ***Via* Groth's Procedure.**—To 13 g. (0.043 mole) of I was added a solution of 2.0 g. (0.086 g.-atom) of sodium in 50-ml. of ethanol. The solution was diluted with 500 ml. of water and treated with a solution containing 20 g. (0.14 mole) of benzoyl chloride in 300 ml. of 0.5 *N* sodium carbonate. Work-up in the manner described by Groth[15] provided a low yield of XXVI (R = C_6H_5), m.p. 168–170°, lit.[15] m.p. 168–169°.

B. Direct Benzoylation of XXVIII.—To a suspension of 2.6 g. (0.0065 mole) of XXVIII, obtained by stepwise addition of 2 equiv. of potassium ethoxide to I, in 30 ml. of ether, was added a solution of 2.5 g. (0.015 mole) of benzoyl chloride in 20 ml. of ether. The white solid was filtered and washed with ether and water to give 3.1 g. (86%) of XXVIa (R = C_6H_5), m.p. 190–192°. The ultraviolet spectrum of the dibenzoate exhibited a maximum at 248 mμ (ϵ 47,200).

Anal. Calcd. for $C_{30}H_{32}O_4S_2$: C, 70.56; H, 4.34; S, 12.56. Found: C, 70.19; H, 4.30; S, 12.54.

When the dipotassio salt XXVIII was prepared according to the procedure of Groth[15] and treated with benzoyl chloride in ether, an 85% yield of XXVIa (R = C_6H_5), m.p. 190–192°, was obtained.

Formation of 2,3-Diacetylthio-1,4-diphenyl-1,4-butanedione (XXVIb, R = CH_3).—To a suspension of 1.9 g. (0.005 mole) of XXVIII in 30 ml. of ether was added 3 ml. of acetyl chloride. The solid was filtered, washed with water, and dried. Recrystallization from a methylene chloride–ether mixture gave 0.8 g. (42%) of colorless crystals, XXVIb, m.p. 200–204°.

Anal. Calcd. for $C_{20}H_{18}O_4S_2$: C, 62.19; H, 4.69; S, 16.58. Found: C, 61.90; H, 4.84; S, 16.76.

The n.m.r. spectrum of the diacetate exhibited two singlets at τ 4.02 (1 proton) and 7.71 (2.96 protons) in addition to an aromatic multiplet (15 protons).

Preparation of 2,3-Diacetylthio-1,4-diphenyl-1,4-butanedione (XXVIb, R = CH_3).—Dibenzoylacetylene (2.34 g. 0.01 mole) was mixed with 0.5 g. of dibenzoyl peroxide and 3.04 g. (0.04 mole) of thiolacetic acid. After complete solution (1 hr. at room temperature), the solution was dried *in vacuo* and dissolved in ether. The ether solution was washed with 1% sodium bicarbonate solution and then water. The ether layer was dried and evaporated; the oily solid was washed with 25 ml. of cold ether and filtered. The residue (0.25 g.) crystallized from an ether–pentane mixture, darkened at 138–140°, m.p. 189–190°.

Anal. Calcd. for $C_{20}H_{18}O_4S_2$: C, 62.19; H, 4.69; S, 16.58. Found: C, 62.04; H, 4.75; S, 16.26.

The n.m.r. spectrum exhibited singlets at τ 4.08 (1 proton) and 7.70 (3 protons) and an aromatic multiplet (15 protons). The infrared spectrum of this material was identical with the diacetate obtained from XXVIII with the exception of additional peaks at 1300, 1250, and 1150 cm.$^{-1}$.

Desulfurization of 1,4-Diphenyl-2,3-dibenzoylthio-1,4-butanedione (XXVIa, R = C_6H_5).—A suspension of 2.0 g. (3.9 mmoles) of XXVIa (R = C_6H_5) and two teaspoonfuls of Raney nickel was stirred at reflux for 18 hr. Work-up in the usual manner gave 0.6 g. (66%) of V, m.p. 143–145°, and 0.4 g. of an oil. Analysis of the oil in the vapor fractometer indicated benzyl alcohol as the only volatile component.

Desulfurization of I.—To a suspension of 2.0 g. (6.6 mmoles) of I in 30 ml. of ethanol was added 1 teaspoonful of Raney nickel. The mixture was stirred at reflux for 48 hr. Work-up in the usual manner provided 0.115 g. (7%) of V, m.p. 137–143°, and 0.25 g. of oil. The ethanol distillate was treated with 2,4-dinitrophenylhydrazine and afforded 0.435 g. of the 2,4-dinitrophenylhydrazone of acetophenone, m.p. 248–251°, lit.[31] m.p. 250°.

Cleavage of I with Sodium Methoxide and Determination of the Rate of Appearance of Acetophenone.—The disulfide (I, 0.03 mole) was cleaved with 1 equiv. of sodium methoxide in methanol. One-milliliter aliquots were withdrawn at the indicated time intervals, acidified with methanolic hydrochloride acid, and analyzed in the vapor fractometer for acetophenone (see Table IV). A column of 4% Carbowax 400 on Chromosorb P (30–40 mesh) was used. The column was maintained at 100° with a helium flow rate of 40.2 cc./min. Distilled nitrobenzene was used as an internal standard.

TABLE IV

Time, hr.	% acetophenone	Time, hr.	% acetophenone
0.66	4.1	12.0	10.5
2.0	4.6	48.0	12.5
6.0	6.9	72.0	13.8

The rate of appearance of acetophenone from the cleavage of I with 0.5 equiv. of sodium methoxide in methanol is shown in Table V.

TABLE V

Time, hr.	% acetophenone	Time, hr.	% acetophenone
0.5	1.7	72	16.8
4.0	5.4	96	16.8
28.0	12.4	150	16.9
47.0	13.7		

The rate of appearance of acetophenone from the cleavage of I with 0.25 equiv. of sodium methoxide in methanol is shown in Table VI.

TABLE VI

Time, hr.	% acetophenone	Time, hr.	% acetophenone
1.5	1.5	22	1.9
5.5	2.3	80	13.9

Cleavage of 1,5-Diphenyl-3-thia-1,5-pentanedione (XXIV) with Potassium Ethoxide.—To a solution of 2.94 g. (0.035 mole) of potassium in 20 ml. of ethanol was added 9 g. (0.033 mole) of XXIV. A crystalline precipitate formed almost immediately. After 72 hr. at room temperature, 2.59 g. of a salt, m.p. 155–165°, was obtained. Upon acidification, the salt was converted into a ketonic product, m.p. 122–124° dec., with evolution of hydrogen sulfide. Ethanol was removed from the reaction mixture, and the residue was partitioned between ether and water. The ether solution was dried and evaporated to an oil which afforded 1.0 g. of acetophenone on distillation. Acidification of the aqueous layer gave 3.0 g. of a polymeric yellow solid which was not identified.

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[31] R. L. Shriner, R. L. Fuson, and D. Y. Curtain, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 113.