17. *Organic Sulphur Compounds. Part XXVII. The Relation between the Constitution of Thioethers and Thiols and their Sensitivity towards Alkali.*

By Alexander Schönberg and Youssef Iskander.

Whereas the thioethers listed in Table I are remarkably stable towards alkali, the nitro-derivatives (Table II) are extremely sensitive. The latter compounds are all characterised by the group $p\text{-}\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}SR}$ or by such groups in which the hydrogen in the methylene group is partially or completely substituted. The mechanism of the hydrolysis is discussed (schemes A and B). *Didesyl sulphide* (XII) was obtained in two isomeric forms. Both are very sensitive towards alkali (scheme C); the same is true of *desylthiol* (XIV) (scheme F). As may be seen from schemes F and D, it is believed that the action of alkali on β-keto-thiols, the corresponding thioethers, and β-ketothiocarboxylic acids, which are highly sensitive to alkali, proceeds in such a way that water or the alkali hydroxide is added to the carbonyl group, and the hydrate so formed decomposes. There is no general parallelism between thermolability of thioethers and their sensitivity towards alkali, since the thermolabile phenyl triphenylmethyl sulphide is very stable towards alkali; on the other hand, didesyl sulphide is thermolabile (formation of the blue thiobenzil; scheme E) and is also very sensitive to alkali.

Dimethyl sulphide is only partially hydrolysed when heated with 3N-alkali at 260° for two hours (Billheimer and Reid, *J. Amer. Chem. Soc.*, 1930, **52**, 4338), but two classes of its derivatives, the β- and the γ-ketothio-carboxylic acids, are very sensitive to the action of alkali (Nicolet, *J. Amer. Chem. Soc.*, 1931, **53**, 3067; Behaghel and Ratz, *Ber.*, 1939, **72**, 1257), the former undergoing hydrolysis and the latter decomposition :

$$\mathrm{Ph{\cdot}CO{\cdot}CHPh{\cdot}S{\cdot}CH_2{\cdot}CO_2H \xrightarrow{H_2O} Ph{\cdot}CO{\cdot}CH_2Ph + OH{\cdot}S{\cdot}CH_2{\cdot}CO_2H}$$

$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}S{\cdot}CH_2{\cdot}CO_2H \longrightarrow Ph{\cdot}CO{\cdot}CH{:}CHPh + SH{\cdot}CH_2{\cdot}CO_2H}$$

This paper deals with *p*-nitrobenzyl thioethers (Table II), one ββ'-diketo-thioether (XII) and the corresponding thiol (XIV), which are all highly sensitive to alkali.

Part I.

Sensitivity of p-*Nitrobenzyl Thioethers towards Alkali.*—In Table I are listed a number of substances which, according to our observation, are affected either only slightly or not at all by 1 hour's boiling in 5% alkali solution, in which they are all soluble. In contrast, the substances listed in Table II are completely or almost completely hydrolysed when heated for 5 minutes in 5% alkali solution, in which they are all soluble.

Table I.

(I.)	$\mathrm{CH_2Ph{\cdot}S{\cdot}CH_2{\cdot}CO_2H}$ [1]	$p\text{-}\mathrm{NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H}$	(II.)
(III.)	$\mathrm{CH_2Ph{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$	$\mathrm{CPh_3{\cdot}S{\cdot}CH_2{\cdot}CO_2H}$ [2]	(IV.)

Table II.

(V.)	$p\text{-}\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H}$	$p\text{-}\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$	(VI.)
(VII.)	$p\text{-}\mathrm{NO_2{\cdot}C_6H_4{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H}$		

Mechanism of the Action of Alkali on the p-*Nitrobenzyl Thioethers.*—For the action of alkali on α-(p-*nitrotriphenylmethylthio*)*acetic acid* (VII), the following scheme is proposed, which shows the addition of sodium hydroxide to the nitro-group, the splitting off of sulphenacetic acid (VIII), and the rearrangement of the remainder to *p*-nitrotriphenylmethane (IX), which separates during the reaction :

$$\text{(A)}\quad \text{(VII.)}\ \mathrm{NO_2{\cdot}C_6H_4{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H \xrightarrow{NaOH} OH{\cdot}NO(ONa){\cdot}C_6H_4{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H \longrightarrow}$$

$$\text{(VIII.)}\ \mathrm{ONa{\cdot}S{\cdot}CH_2{\cdot}CO_2H + OH{\cdot}NO{:}C_6H_4{:}CPh_2 \longrightarrow NO_2{\cdot}C_6H_4{\cdot}CHPh_2}\quad \text{(IX.)}$$

For the saponification of α-(p-*nitrobenzylthio*)*acetic acid* (V), the following scheme, in contrast to the above (saponification of VII), shows as first step, not the addition of sodium hydroxide to the nitro-group, but the formation of a sodium salt of the *aci*-nitro-group. (X) indicates, but only very roughly, an unstable intermediate product. The final product, azobenzaldehyde (XI), separates during the reaction :

$$\text{(B)}\quad \underset{\text{(V.)}}{2p\text{-}\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H}} \xrightarrow{\mathrm{NaOH}} \mathrm{2NO(ONa){:}C_6H_4{:}CH{\cdot}S{\cdot}CH_2{\cdot}CO_2H \longrightarrow}$$

$$\text{(VIII)} + \left[\mathrm{2O\overset{|}{N}{:}C_6H_4{:}\overset{|}{C}H}\right]\text{(X.)} \longrightarrow \mathrm{CHO{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO}\quad \text{(XI.)}$$

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[1] Holmberg, *J. pr. Chem.*, 1934, **141**, 93.

[2] Biilmann and Due, *Bull. Soc. chim.*, 1924, **35**, 384.

Sulphenacetic acid (VIII), which should be formed according to the above scheme, was not isolated, as this substance is very unstable towards alkali. The alkaline solution, after acidification, furnished hydrogen sulphide, which is one of the products of the action of alkali on sulphenacetic acid (Schöberl, *Annalen*, 1933, **507**, 111).

It is suggested that the action of alkali on β-(p-*nitrobenzylthio*)*propionic acid* (VI) is like that on *p*-nitrobenzylthioacetic acid, and one would expect *p*-azobenzaldehyde together with β-sulphenpropionic acid ($OH{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$) to be formed. We obtained the azobenzaldehyde in a very small yield and *p*-azoxybenzaldehyde ($CHO{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}C_6H_4{\cdot}CHO$) and β-dithiodipropionic acid

$$(CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H)$$

in good yield. The formation of the azoxy-compound is explained by the suggestion that the azo-compound first formed is oxidised by the β-sulphenpropionic acid, which in turn is reduced to β-dithiodipropionic acid (compare Price and Twiss, J., 1910, **97**, 1175; Fries, *Ber.*, 1912, **45**, 2965).

Part II.

The Action of Alkali on ββ'-Diketo-sulphides, β-Ketothio-carboxylic Acids and β-Keto-thiols.—(1) *Action of alkali on didesyl sulphide* (XII). This substance occurs in two probably stereoisomeric forms, which are completely or almost completely hydrolysed by aqueous alcoholic alkali (3%) after 5 minutes' boiling, deoxybenzoin and, after acidification, sulphur being obtained :

$$\text{(C)}\quad \text{(XII.)}\ Ph{\cdot}CO{\cdot}CHPh{\cdot}S{\cdot}CHPh{\cdot}COPh + 2H_2O \longrightarrow 2Ph{\cdot}CO{\cdot}CH_2Ph + S(OH)_2$$

$$2S(OH)_2 \longrightarrow H_2O + H_2S_2O_3 \xrightarrow{\text{acid}} H_2SO_3 + S$$

[With regard to the decomposition of $S(OH)_2$, see Förster, Lange, Drossbach, and Seidel, *Z. anorg. Chem.*, 1923, **128**, 268.]

(2) *Mechanism of the action of alkali on β-ketothio-carboxylic acids and ββ'-diketo-sulphides.* It is suggested that the first step is the formation of a hydrate, which is decomposed in accordance with scheme D (A and B are univalent groups; in the case of β-ketothio-carboxylic acids, R is an aliphatic acid group, *e.g.*, $CH_2{\cdot}CO_2H$) :

$$\text{(D)}\quad R'{\cdot}CO{\cdot}CAB{\cdot}SR \longrightarrow R'{\cdot}C(OH)_2{\cdot}CAB{\cdot}SR \longrightarrow OH{\cdot}SR + R'{\cdot}C(OH){:}CAB \longrightarrow R'{\cdot}CO{\cdot}CHAB$$

According to this suggestion the degree of susceptibility towards alkali of sulphides which have a carbonyl group in the β-position depends on the tendency to form hydrates and on their instability, *i.e.*, on the velocity of the decomposition reaction.

The fission of α-(benzoylbenzhydrylthio)acetic acid (XIII) by alkali in two different directions (Behaghel and Ratz, *Ber.*, 1939, **72**, 1275) may also be explained by hydrate formation :

$$\begin{tikzcd}
 & & Ph{\cdot}CO{\cdot}CHPh_2 + OH{\cdot}S{\cdot}CH_2{\cdot}CO_2H \\
\underset{\text{(XIII.)}}{Ph{\cdot}CO{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H} \arrow[r] & Ph{\cdot}C(OH)_2{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H \arrow[ur, "a"] \arrow[dr, "b"'] & \\
 & & Ph{\cdot}CO_2H + CHPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H
\end{tikzcd}$$

Scheme *b* resembles the cleavage of a non-enolisable ketone by the action of sodamide (Schönberg, *Annalen*, 1924, **436**, 206) :

$$COPh_2 + NaNH_2 \longrightarrow CPh_2(ONa){\cdot}NH_2 \xrightarrow{\text{decomp.}} PhH + Ph{\cdot}CO{\cdot}NHNa.$$

In the case of (XIII), the formation of deoxybenzoin (scheme *a*) is the main reaction. On the other hand, β-(*benzoylbenzhydrylthio*)*propionic acid*, $Ph{\cdot}CO{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, and *phenyl α-benzoylbenzhydryl sulphide*, $Ph{\cdot}CO{\cdot}CPh_2{\cdot}SPh$, yield mainly β-(*benzhydrylthio*)*propionic acid*, $CHPh_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, and phenyl benzhydryl sulphide, $CHPh_2{\cdot}SPh$, respectively, in accordance with scheme *b*.

(3) *Relationship between thermolability of thioethers and sensitivity towards alkali.* There is no general parallelism. For instance, phenyl triphenylmethyl sulphide is rather unstable towards heat (decomposition into diphenyl disulphide and triphenylmethyl; Schönberg and co-workers, *Ber.*, 1929, **62**, 2552), but is completely or almost completely resistant to boiling with aqueous-alcoholic alkali (5%) for four hours. On the other hand, either of the two stereoisomeric forms of didesyl sulphide (XII) decomposes above its melting point with formation of a blue compound, believed to be thiobenzil (Schönberg and Schütz, *Annalen*, 1927, **454**, 53) :

$$\text{(E)}\quad Ph{\cdot}CO{\cdot}CHPh{\cdot}S{\cdot}CHPh{\cdot}COPh \longrightarrow Ph{\cdot}CO{\cdot}CSPh + Ph{\cdot}CH_2{\cdot}COPh$$

Saponification of (XII) yields benzilic acid as a by-product, produced probably by the benzilic acid rearrangement of thiobenzil.

(4) *Action of alkali on* β-*keto-thiols.* The action of alkali on β-keto-thiols whereby the thiol group is easily replaced by hydrogen with the liberation of sulphur, observed by Groth (*Chem. Zentr.*, 1924, I, 1038) in the case of phenacylthiol, was observed by us when *desylthiol* (XIV) or its *benzoate* was heated with 2·5% alcoholic alkali for 10 minutes, giving deoxybenzoin and, after acidification, sulphur. Scheme F shows the analogy with the action of alkali on thioethers (see above).*

$$\text{(F)}\quad \underset{\text{(XIV.)}}{\text{Ph·CO·CHPh·SH}} \xrightarrow{H_2O} \text{Ph·C(OH)}_2\text{·CHPh·SH} \longrightarrow \text{Ph·CO·CH}_2\text{Ph} + \text{SH·OH} \longrightarrow H_2O + S.$$

On the other hand, α-*benzoylbenzhydrylthiol* (XV) is more stable to alkali than (XIV), since it can be prepared in good yield by the action of alkali on the corresponding *thiobenzoate* (XVI) :

$$\text{Ph·CO·CPh}_2\text{·S·COPh (XVI)} \xrightarrow{H_2O} \text{Ph·CO·CPh}_2\text{·SH (XV)} + \text{Ph·CO}_2\text{H}$$

EXPERIMENTAL.

Part I.

α-(p-*Nitrobenzylthio*)*acetic Acid* (V).—*p*-Nitrobenzyl chloride (4·3 g.), dissolved in alcohol (100 c.c.), was treated with a solution of thiolacetic acid (2·5 g.) and sodium bicarbonate (5 g.) in water (20 c.c.) and the mixture boiled on the water-bath for 1 hour. Cooling, dilution with water, filtration, and acidification gave a colourless crystalline *acid* (4·5 g.), which separated from dilute alcohol or carbon tetrachloride in colourless scales, m. p. 114° (Found : C, 48·1 ; H, 3·7 ; N, 6·3 ; S, 14·1. $C_9H_9O_4NS$ requires C, 47·6 ; H, 4·0 ; N, 6·2 ; S, 14·1%).

Alkaline hydrolysis. The acid (2 g.) was dissolved in 5% sodium hydroxide solution (50 c.c.) and boiled for 5 minutes. The solid obtained (1·1 g.) was washed with water and crystallised from glacial acetic acid, giving orange-red crystals, m. p. 230—235° alone or mixed with *p*-azobenzaldehyde (Freundler, *Bull. Soc. chim.*, 1904, **31**, 453) (Found : C, 70·3 ; H, 4·2 ; N, 11·9. Calc. for $C_{14}H_{10}O_2N_2$: C, 70·5 ; H, 4·2 ; N, 11·8%). On acidification of the alkaline filtrate, hydrogen sulphide was evolved.

β-(p-*Nitrobenzylthio*)*propionic Acid* (VI).—Prepared from *p*-nitrobenzyl chloride (4·3 g.) and β-thiolpropionic acid (2·7 g.) by the method described above, and isolated in a similar way, the *acid* (4·5 g.) crystallised from dilute alcohol in colourless needles, m. p. 104—105° (Found : C, 50·0 ; H, 4·6 ; N, 5·8 ; S, 13·5. $C_{10}H_{11}O_4NS$ requires C, 49·8 ; H, 4·6 ; N, 5·8 ; S, 13·3%).

Alkaline hydrolysis. The acid (2 g.) was hydrolysed as described above. The solid obtained (1·1 g.) crystallised from benzene in yellow needles, m. p. 190° alone or mixed with *p*-azoxybenzaldehyde (Human and Weil, *Ber.*, 1903, **36**, 3474) (Found : C, 66·1 ; H, 3·9 ; N, 11·0. Calc. for $C_{14}H_{10}O_3N_2$: C, 66·1 ; H, 3·9 ; N, 11·0%). On acidification of the alkaline filtrate, hydrogen sulphide was not evolved and a dark solid was slowly precipitated. This was collected, dried, boiled with carbon tetrachloride to remove any unchanged acid, and crystallised from hot water, giving β-dithiodipropionic acid, m. p. 155° alone or mixed with an authentic specimen (Biilmann, *Annalen*, 1905, **339**, 365).

The acids (V) and (VI) were completely hydrolysed in 5% sodium hydroxide solution in 24 hours at room temperature.

α-(p-*Nitrotriphenylmethylthio*)*acetic Acid* (VII).—*p*-Nitrotriphenylchloromethane (3·5 g.), dissolved in dry toluene (30 c.c.), was treated with thiolacetic acid (1 g.), and the solution boiled for 1 hour until no more hydrogen chloride was evolved. Ether (30 c.c.) was added, and the p-*nitrotriphenylmethylthioacetic acid* extracted with sodium bicarbonate solution. The viscous acid (3·6 g.) obtained on acidification solidified over-night in the ice chest and separated from benzene–light petroleum (b. p. 60—70°) in colourless crystals, m. p. 153—155° (Found : C, 65·7 ; H, 4·4 ; N, 3·9. $C_{21}H_{17}O_4NS$ requires C, 66·5 ; H, 4·5 ; N, 3·7%).

Alkaline hydrolysis. The acid (0·34 g.) was treated with 5% sodium hydroxide solution (20 c.c.) in the cold with the formation of a yellow solid (probably the sodium salt). After 5 minutes' boiling, the liberated oily substance was extracted from the red liquid with ether and proved to be *p*-nitrotriphenylmethane (0·26 g.), m. p. 97°, not depressed by an authentic specimen, m. p. 94° (Baeyer and Lohr, *Ber.*, 1890, **23**, 1622). Acidification of the alkaline liquid gave much hydrogen sulphide.

α-(p-*Aminobenzylthio*)*acetic Acid* (II).—α-(*p*-Nitrobenzylthio)acetic acid (1·5 g.) was heated with concentrated hydrochloric acid (10 c.c.) and granulated tin (3 g.) on the water-bath until all the tin had dissolved. The excess of hydrochloric acid was evaporated on the water-bath, the viscous residue dissolved in water (100 c.c.) and freed from tin with hydrogen sulphide, and the clear filtrate evaporated to dryness on the water-bath. The residual hydrochloride was dissolved in the minimum amount of cold water, and the filtered solution treated with a few drops of aqueous ammonia. While the solution was still very faintly acid to litmus

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* An analogous scheme is proposed for the quantitative and quick replacement of the bromine by hydrogen when α-benzoylbenzhydryl bromide is heated with hydrogen bromide in acetic acid (Löwenbein and Schuster, *Annalen*, 1930, **481**, 117) :

$$\text{Ph·CO·CBrPh}_2 + \text{HBr} \longrightarrow \text{Ph·CBr(OH)·CBrPh}_2 \longrightarrow \text{Br}_2 + \text{Ph·C(OH)⁚CPh}_2 \longrightarrow \text{Ph·CO·CHPh}_2$$

the *amino-acid* was precipitated; it separated from alcohol in colourless crystals, m. p. 155—156°, soluble in water and alcohol and, with difficulty, in ether and benzene (Found: C, 55·1; H, 5·4; N, 6·7; S, 16·2. $C_9H_{11}O_2NS$ requires C, 54·8; H, 5·6; N, 7·1; S, 16·2%). The acid was recovered unchanged after 20 minutes' boiling with 5% sodium hydroxide solution. On diazotisation and coupling with β-naphthol it gave a dark red dye.

Part II.

β-(*Benzylthio*)*propionic Acid* (III).—Benzyl chloride (2·53 g.), dissolved in alcohol (50 c.c.), was treated with a solution of β-thiolpropionic acid (2·1 g.) and sodium bicarbonate (4 g.) in water (20 c.c.), and the mixture boiled on the water-bath for 1 hour. Cooling, dilution with water, washing with ether, and acidification gave an oily acid (3·5 g.), which solidified in the ice-chest. It crystallised from light petroleum (b. p. 60—70°) in colourless plates, m. p. 82—83° (Mörner, *Z. physiol. Chem.*, 1904, **42**, 352, gives m. p. 81·5°). The acid was recovered almost unchanged after 1 hour's boiling with 5% sodium hydroxide solution.

Desylthiol (XIV).—A solution of sodium (2·3 g.) in absolute alcohol (100 c.c.) was treated with excess of hydrogen sulphide for 1 hour at room temperature. The sodium hydrosulphide solution was cooled in ice and treated with finely powdered desyl chloride (23 g.) (*Organic Syntheses*, 1932, **12**, 20) in one addition. A quick reaction occurred with the formation of a colourless microcrystallline solid (11·5 g., m. p. 120—140°) mixed with sodium chloride. The alcoholic filtrate was diluted with ice-water, the liberated oily substance extracted with ether, and the ethereal layer dried over calcium chloride for 1 day. After distillation of the ether the viscous oily residue (11 g.) gave the thiol test (solid sodium nitrite, added to a solution of the thiol in glacial acetic acid, gave a red coloration; Rheinboldt, *Ber.*, 1927, **60**, 184). The lead salt of the thiol was precipitated from ethereal solution by lead acetate, washed with ether, and decomposed with dilute hydrochloric acid. The liberated thiol, isolated by means of ether, solidified in the ice-chest after 1 month. On treatment with a few c.c. of cold alcohol, half the bulk, which was semi-solid, was dissolved, leaving a colourless crystalline solid, m. p. 42—44° (Found: C, 73·8; H, 5·4; S, 13·8. $C_{14}H_{12}OS$ requires C, 73·7; H, 5·3; S, 14·0%). A solution of the thiol in alcohol reacted with iodine in potassium iodide; the expected disulphide could not be obtained crystalline.

Alkaline hydrolysis. The thiol (2 g.), dissolved in alcohol (60 c.c.), was treated with 10% sodium hydroxide solution (20 c.c.), and the mixture boiled for 10 minutes. Dilution with ice-water precipitated deoxybenzoin (1·2 g.), m. p. 58—60°; the filtrate, on acidification, gave hydrogen sulphide and a yellowish-white emulsion, which was extracted with ether. Evaporation of the ether left sulphur (0·2 g.), m. p. 118—120° after being washed with alcohol.

Desyl Thiobenzoate.—(1) A solution of desyl chloride (17·4 g.) and potassium thiobenzoate (Kym, *Ber.*, 1899, **32**, 3533) (13·4 g.) in absolute alcohol (400 c.c.) was boiled for 10 minutes, potassium chloride being precipitated. After cooling, a colourless crystalline substance separated, which was washed with water and recrystallised from alcohol. Yield 25 g., m. p. 110—112° (Found: C, 75·9; H, 5·0; S, 9·6. $C_{21}H_{16}O_2S$ requires C, 75·9; H, 4·8; S, 9·6%).

(2) Desylthiol (0·5 g.), dissolved in pyridine (2 c.c.), was treated with benzoyl chloride (0·25 c.c.); after 5 minutes, the mixture was cooled and acidified with cold dilute sulphuric acid. The liberated oily substance, after decantation from the aqueous layer, was treated with hot alcohol; on cooling, a crystalline solid (0·5 g.) was precipitated, m. p. 110—112° alone or mixed with the *desyl thiobenzoate* prepared by method (1).

Alkaline hydrolysis. Desyl thiobenzoate (10 g.), dissolved in boiling alcohol (300 c.c.), was treated with 10% sodium hydroxide solution (100 c.c.) and boiled for 5 minutes. Ice-water was then added; the precipitated deoxybenzoin (5·2 g.) was removed, the filtrate acidified and extracted with ether, and the ethereal layer washed with sodium bicarbonate solution. The bicarbonate layer, after acidification, gave benzoic acid and hydrogen sulphide; the ether contained about 1 g. of a viscous liquid contaminated with a yellow solid, which was isolated by the addition of alcohol. It crystallised from benzene–absolute alcohol, and proved to be sulphur, m. p. 118—120°.

Didesyl Sulphide (XII).—The solid, m. p. 120—140°, obtained in the preparation of desylthiol (see above) separated from benzene–absolute alcohol in colourless needles (5·5 g.), m. p. 168—169° (Found: C, 79·9; H, 5·3; S, 7·6. $C_{28}H_{22}O_2S$ requires C, 79·6; H, 5·2; S, 7·6%). The mother-liquor, after concentration and evaporation of the benzene, deposited a substance (4·5 g.), which crystallised from absolute alcohol in long colourless needles, m. p. 128—129° (Found: C, 79·5; H, 5·3; S, 7·7%). The two substances are both *didesyl sulphide*; it is suggested that one of them is the racemic form, and the other, the *meso*-form. Both forms were partly dissolved in hot alcohol; after cooling, the supersaturated solutions were immediately treated with a few drops of 10% sodium hydroxide solution. An immediate yellow or orange colour (according to concentration) was developed. Both forms, when heated above the m. p., gave a blue melt (formation of thiobenzil; Schönberg and Schütz, *Annalen*, 1927, **454**, 53).

Alkaline hydrolysis. Didesyl sulphide (4 g.), m. p. 169°, dissolved in boiling alcohol (100 c.c.), was treated with 10% sodium hydroxide solution (40 c.c.) and boiled for 5 minutes. When ice-water was added in excess, deoxybenzoin (2·9 g.) was precipitated. The filtrate was acidified, and the liberated oily substance extracted with ether; sodium bicarbonate removed benzilic acid from the extract. The ether, after evaporation, left a viscous oily substance contaminated with sulphur, which was separated by washing with alcohol.

The same result was obtained by the hydrolysis of the form, m. p. 129°.

β-(*Desylthio*)*propionic Acid*.—Desyl chloride (4·6 g.) and β-thiolpropionic acid (2·1 g.) were heated on the water-bath for 6 hours until no more hydrogen chloride was evolved. The addition of benzene caused the precipitation of β-dithiodipropionic acid, m. p. 155°. A few c.c. of petroleum (b. p. 60—70°) were added to the filtrate, and the β-(*desylthio*)*propionic acid* extracted with sodium bicarbonate solution. Acidification of the bicarbonate layer liberated the acid as an oil which solidified on standing; it crystallised from dilute methyl alcohol in micro-needles, m. p. 108—109° (Found: C, 68·0; H, 5·5; S, 10·9. $C_{17}H_{16}O_3S$ requires C, 68·0; H, 5·3; S, 10·7%).

Comparative Experiment on the Hydrolysis of α-(*Desylthio*)*acetic Acid and* β-(*Desylthio*)*propionic Acid*.—The two acids (0·2 g. of each) in two test tubes were each treated with 5% sodium hydroxide solution (5 c.c.) and heated on the water-bath. Ths solution of desylthioacetic acid became turbid even in the cold, that of the other acid only after 3·5 minutes; the heating was then stopped, and the products immediately cooled. The first turbid solution deposited deoxybenzoin (compare Behaghel and Schneider, *Ber.*, 1935, **68**, 1588). The other alkaline solution, on acidification, gave β-(desylthio)propionic acid in almost quantitative yield. Treatment of this acid with the hot sodium hydroxide solution for 20 minutes caused partial hydrolysis (about 15%), with the formation of deoxybenzoin.

Desyl Phenyl Sulphide.—Desyl chloride (4·6 g.) was added to an alcoholic solution of thiophenol (2·2 g.) and sodium ethoxide (0·46 g. of sodium in 20 c.c. of absolute alcohol); the mixture was boiled for 10 minutes. Water in sufficient amount to dissolve the precipitated sodium chloride was added, and the mixture cooled in ice; desyl phenyl sulphide was precipitated in good yield. It crystallised from petroleum (b. p. 60—70°) in long colourless needles, m. p. 83—84° (Found: C, 78·9; H, 5·4; S, 10·5. Calc. for $C_{20}H_{16}OS$: C, 78·9; H, 5·3; S, 10·5%) (Mitchell and Smiles, J., 1933, 1529, give m. p. 81°).

Alkaline hydrolysis. Desyl phenyl sulphide (0·5 g.), dissolved in hot alcohol (50 c.c.), was treated with 10% sodium hydroxide solution (5 c.c.) and boiled for ½ hour. The mixture was cooled, diluted with water, and extracted with ether. When the alkaline solution was acidified, a strong smell of thiophenol was noticed; the ether contained most of the original substance.

α-*Benzoylbenzhydryl Thiobenzoate* (XVI).—Benzoyldiphenylchloromethane (Löwenbein and Schuster, *Annalen*, 1930, **481**, 114) (10·2 g.), dissolved in boiling absolute alcohol (100 c.c.), was treated with potassium thiobenzoate (5·9 g.) (compare Kym, *loc. cit.*) in absolute alcohol (100 c.c.) and boiled for 10 minutes. Sufficient water to dissolve the potassium chloride was added; on cooling, an oily substance was precipitated which solidified on standing. It separated from absolute alcohol in colourless crystals (5 g.), m. p. 129—130° (Found: C, 79·3; H, 5·1; S, 7·9. $C_{27}H_{20}O_2S$ requires C, 79·4; H, 4·9; S, 7·8%).

α-*Benzoylbenzhydrylthiol* (XV).—α-Benzoylbenzhydryl thiobenzoate (20 g.), dissolved in boiling alcohol (200 c.c.), was treated with 10% sodium hydroxide solution (150 c.c.) and boiled for 10 minutes. The dark yellow solution was cooled, diluted with water, and extracted with ether. The alkaline solution was acidified, and the liberated oily substance extracted with ether. The ethereal layer was washed with sodium bicarbonate solution; acidification of the bicarbonate washings liberated benzoic acid. The ether contained an oily substance which solidified at once (yield, 9 g.); it separated from dilute alcohol in micro-needles, m. p. 98—101°. The thiol test gave a red coloration (Found: C, 78·6; H, 5·5; S, 10·3. $C_{20}H_{16}OS$ requires C, 78·9; H, 5·3; S, 10·5%).

Di-α-benzoylbenzhydryl Disulphide.—α-Benzoylbenzhydrylthiol, dissolved in the necessary amount of hot acetic acid, was treated with the equivalent amount of ferric chloride solution and boiled for 10 minutes. On cooling, a colourless amorphous solid was precipitated; it separated from chloroform–alcohol or from much absolute alcohol in colourless crystals, m. p. 150—154° (Found: C, 79·2; H, 4·9; S, 10·5. $C_{40}H_{30}O_2S_2$ requires C, 79·2; H, 4·9; S, 10·6%).

α-(*Benzoylbenzhydrylthio*)*acetic Acid* (XIII).—Benzoyldiphenylchloromethane (15·3 g.) was treated with thiolacetic acid (4·6 g.) and heated on the water-bath for 2 hours until no more hydrogen chloride was evolved. Dry benzene was added and a few c.c. of petroleum (b. p. 60—70°), causing a slight precipitation of dithiodiacetic acid, m. p. 108°. From the filtrate, a few crystals of benzoyldiphenylmethane, m. p. 136°, separated overnight; these were removed, and (XIII) extracted with sodium bicarbonate solution. Acidification liberated the acid as a viscous oil, which crystallised from benzene–petroleum (b. p. 60—70°) in large particles, m. p. 132—134°; it was recrystallised from dilute alcohol (Found: C, 72·9; H, 5·2; S, 8·8. Calc. for $C_{22}H_{18}O_3S$: C, 72·9; H, 5·0; S, 8·8%).

Behaghel and Ratz (*Ber.*, 1939, **72**, 1275) found that the alkaline hydrolysis of (XIII) gave α-(benzhydrylthio)acetic acid; they gave the m. p. as 218° (probably a misprint for 128°, the correct m. p.).

β-(*Benzoylbenzhydrylthio*)*propionic Acid*.—Benzoyldiphenylchloromethane (9·2 g.) and β-thiolpropionic acid (3·2 g.) were heated on the water-bath for 6 hours until no more hydrogen chloride was evolved. After cooling, the addition of ether precipitated β-dithiodipropionic acid, m. p. 155°. β-(*Benzoylbenzhydrylthio*)-*propionic acid* was extracted from the ethereal solution with sodium bicarbonate solution and liberated on acidification as a viscous substance which solidified after decantation of the aqueous layer and treatment with 50% methyl alcohol. It crystallised from dilute methyl alcohol in small scales, m. p. 134—136° (Found: C, 73·5; H, 5·2; S, 8·6. $C_{23}H_{20}O_3S$ requires C, 73·4; H, 5·3; S, 8·5%).

Alkaline hydrolysis. The acid was boiled with 7% sodium hydroxide solution for 20 minutes. On cooling and dilution with water, a minute quantity of substance was precipitated. This was removed, and acidification of the filtrate gave a substance, which separated from dilute alcohol in colourless crystals of β-(*benzhydrylthio*)*propionic acid*, m. p. 89—90° (Found: C, 70·8; H, 6·2; S, 12·0. $C_{16}H_{16}O_2S$ requires C, 70·6; H, 5·9; S, 11·8%).

Phenyl α-Benzoylbenzhydryl Sulphide.—Benzoyldiphenylchloromethane (3·07 g.) and thiophenol (1·1 g.) in dry toluene (20 c.c.) were boiled for 1 hour until no more hydrogen chloride was evolved. Most of the toluene was distilled off under reduced pressure, and light petroleum (b. p. 50—60°) and a few c.c. of benzene added. After cooling in the ice-chest for some time, a colourless solid was precipitated, which separated from absolute alcohol or benzene–petroleum in colourless crystals, m. p. 119° (Found: C, 82·2; H, 5·2; S, 8·5. $C_{26}H_{20}OS$ requires C, 82·1; H, 5·3; S, 8·4%).

Alkaline hydrolysis. A solution of the sulphide (0·5 g.) in alcohol (50 c.c.) was treated with 10% sodium hydroxide solution (5 c.c.), boiled for 10 minutes, cooled, diluted with water, and kept in the ice-chest overnight. The precipitated solid crystallised from dilute alcohol in long colourless needles, m. p. 78—79° alone or mixed with phenyl benzhydryl sulphide (Finzi and Bellavita, *Gazzetta*, 1932, **62**, 699). Acidification of the mother-liquor produced the smell of thiophenol.

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[*Received, June 6th*, 1941.]