311. *The Anionic Nature of the Desyl and the α-Benzoylbenzhydryl Radical as compared with the Cationoid Reactivity of the Triphenylmethyl Radical. The Hydrolysis of Thio-esters.*

By YOUSSEF ISKANDER.

The thio-ethers (R·SZ) and thiols (R·SH) of the desyl and the α-benzoylbenzhydryl radical (Schönberg and Iskander, *J.*, 1942, 90), which were found to be very easily hydrolysed by alkalis giving RH + Z·S·OH, were found to resist the action of boiling alcoholic hydrochloric acid, and when hydrolysed with concentrated sulphuric acid gave also RH + Z·S·OH; on the other hand, the corresponding thiols and thio-ethers with a triphenylmethyl radical, which are very stable towards alkalis, were found to be easily attacked by concentrated sulphuric acid, giving R·OH + Z·SH. Thus, the anionoid reactivity of the former radicals as compared with the cationoid reactivity of the triphenylmethyl radical were the influencing factors in obtaining two different types of acidic hydrolyses of the corresponding thiobenzoates (cf. *Nature*, 1945, **155**, 141).

THE desyl and the α-benzoylbenzhydryl thiols, thio-ethers, and thio-esters having the general structure COPh·CPhY·SZ (where Y = H or Ph; Z = H, Ph, COPh, $CH_2·CO_2H$, $CH_2·CH_2·CO_2H$, or COPh·CHPh) were found by Schönberg and Iskander (*loc. cit.*) to be hydrolysed by alkalis according to the following schemes :

$$\text{Ph·CO·CPhY·SZ} + H_2O \longrightarrow \text{Ph·CO·CHPhY} + \text{Z·S·OH} \qquad \text{(I.)}$$

or (where Y = Ph and Z = Ph or $CH_2·CH_2·CO_2H$)

$$\text{Ph·CO·CPh}_2\text{·SZ} + H_2O \longrightarrow \text{Ph·CO}_2\text{H} + \text{CHPh}_2\text{·SZ} \qquad \text{(II.)}$$

or a mixture of (I) and (II) where Y = Ph and Z = $CH_2·CO_2H$. In all cases of (I) the radicals have preferred to receive the H of water, thus showing anionoid reactivity.

The present work includes the hydrolysis of these compounds by acids, and the comparison of the results of their hydrolysis with acids or alkalis with those obtained from the action of acids or alkalis on similar structures but with a triphenylmethyl radical.

In all the cases, the triphenylmethyl derivatives resisted the action of alkalis but showed varying degrees of susceptibility to the attack of acids; the products of hydrolysis were always triphenylcarbinol, so the triphenylmethyl radical has acquired the OH of water, thus showing cationoid reactivity : $CPh_3·SZ + H_2O \longrightarrow CPh_3·OH + Z·SH$, where Z = H, Ph, or Ph_3C (see also Vorländer and Mittag, *Ber.*, 1913, **46**, 3452; 1919, **52**, 413; Lecher, *ibid.*, 1915, **48**, 524).

On the other hand, all the desyl and α-benzoylbenzhydryl derivatives were not hydrolysed by aqueous-alcoholic hydrogen chloride, but their products of hydrolysis with concentrated sulphuric acid were the corresponding methane derivatives which were obtained through their alkaline hydrolyses.

The colourless solution of didesyl sulphide (either of the two forms) (Schönberg and Iskander, *loc. cit.*) in absolute alcohol becomes blue on addition of a few drops of water, and after 7 hours' boiling on the water-bath a partial hydrolysis into deoxybenzoin and benzil occurs. The same products were obtained in presence of HCl:

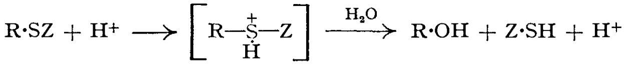
$$(\mathrm{Ph{\cdot}CO{\cdot}CHPh})_2\mathrm{S} + \mathrm{H_2O} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}CH_2Ph} + \mathrm{Ph{\cdot}CO{\cdot}CHPh{\cdot}S{\cdot}OH}$$

$$\mathrm{Ph{\cdot}CO{\cdot}CHPh{\cdot}S{\cdot}OH} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}CSPh}\ \text{(blue thiobenzil)} + \mathrm{H_2O}$$

$$\mathrm{Ph{\cdot}CO{\cdot}CSPh} + \mathrm{H_2O} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}COPh} + \mathrm{H_2S}$$

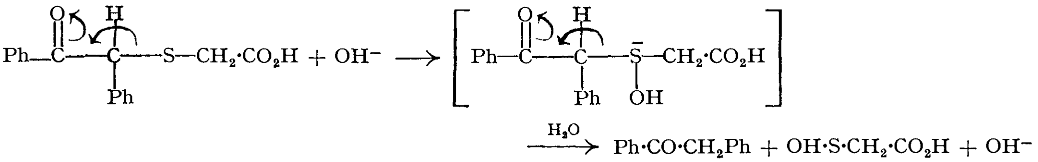
In the alkaline hydrolysis of didesyl sulphide benzilic acid was isolated as a by-product. The above reaction must have been the side reaction of the alkaline hydrolysis, whereby the benzil was changed into benzilic acid. In the main alkaline hydrolysis reaction the sulphur atom has received two OH groups with a subsequent formation of two molecules of deoxybenzoin, while in the neutral or acid hydrolysis and in the side reaction of the alkaline hydrolysis the sulphur atom has received one OH only. Triphenylmethyl sulphide, on the other hand, is very stable towards alkalis but very easily hydrolysed by concentrated sulphuric acid, the sulphur atom receiving two hydrogens, with subsequent formation of triphenylcarbinol (Vorländer and Mittag, *loc. cit.*).

It seems, therefore, that the susceptibility of the compounds concerned towards acids depends on the proton affinity of the sulphur atom:



$$\mathrm{R{\cdot}SZ} + \mathrm{H^+} \longrightarrow \left[\mathrm{R{-}}\underset{\mathrm{H}}{\overset{+}{\mathrm{S}}}\mathrm{{-}Z}\right] \xrightarrow{\mathrm{H_2O}} \mathrm{R{\cdot}OH} + \mathrm{Z{\cdot}SH} + \mathrm{H^+}$$

while the OH which has its full quota of electrons could not approach the sulphur atom except after that atom has become deficient in electrons by electromeric displacements towards the carbonyl group of the β-keto-thiols and thio-ethers or towards the nitro-group in the *p*-nitrobenzylthio-acids * (Schönberg and Iskander, *loc. cit.*):



And in cases where the alkaline hydrolysis was hindered (scheme II) the sulphur atom must have remained rich with its electrons under the influence of the extra phenyl group and the length of the chain, with a subsequent normal attack of the alkali on the carbonyl group and the elimination of the benzoyl group. The effect of the phenyl group must have also been the cause of the stability of the α-benzoylbenzhydrylthiol as compared with desylthiol (Schönberg and Iskander, *loc. cit.*) and phenacylthiol (Groth, *Centr.*, 1924, I, 1039).

EXPERIMENTAL

Hydrolysis of Triphenylmethyl Thiobenzoate (Vorländer and Mittag, *Ber.*, 1913, **46**, 3452).—(a) *Alkaline hydrolysis.* The thiobenzoate (1 g.), dissolved in alcohol (20 c.c.), was treated with 10% sodium hydroxide solution (10 c.c.), and the mixture boiled on the water-bath for 5 mins. The resulting solution was diluted with water, acidified, and the liberated oil extracted with ether. The ethereal layer, after being washed with sodium hydrogen carbonate solution, contained an oily substance which after solidification had m. p. 107° alone or mixed with an authentic specimen of triphenylmethylthiol. The bicarbonate washings, after acidification, liberated benzoic acid.

(b) *Acid hydrolysis.* The thiobenzoate (1·2 g.), dissolved in boiling alcohol (200 c.c.), was treated with concentrated hydrochloric acid (30 c.c.) and boiled for 15 mins. The colour changed at once to yellow and there was an odour of hydrogen sulphide. Water was then added, and the liberated oil extracted with ether. The ethereal layer, which was yellow, became colourless when washed with sodium hydrogen carbonate solution, and afforded a colourless substance, m. p. 164° alone or mixed with

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* Work by Iskander and Riad shows that *a*-*m*-nitrobenzylthioacetic acid resists the action of alkalis, thus proving that electromeric displacements causing a withdrawal of electrons from the sulphur atom must precede the alkaline hydrolysis.

triphenylcarbinol. The yellow bicarbonate washings, on acidification, liberated an oily acid which was proved to be thiobenzoic acid by oxidation with iodine solution and identity of the product with dibenzoyl disulphide, m. p. and mixed m. p. 133°.

Acid Hydrolysis of α-Benzoylbenzhydryl Thiobenzoate (Schönberg and Iskander, *loc. cit.*).—(*a*) The thiobenzoate (2 g.) in boiling alcohol (200 c.c.) was treated with concentrated hydrochloric acid (30 c.c.), and the mixture boiled on the water-bath for 2 hours. After dilution with water, extraction with ether, and washing with sodium hydrogen carbonate solution, the ether yielded a colourless substance, m. p. 98° alone or mixed with α-benzoylbenzhydrylthiol, and the bicarbonate washings contained benzoic acid.

(*b*) The thiobenzoate (0·1 g.) was dissolved in concentrated sulphuric acid (10 c.c.), and the solution set aside for 5 mins. The resulting blue solution, on dilution with water, precipitated a colourless solid, m. p. 150—154° alone or mixed with di-α-benzoylbenzhydryl disulphide.

Desyl thiobenzoate (Schönberg and Iskander, *loc. cit.*) resisted the attack of boiling alcoholic hydrogen chloride for 6 hours.

Acid Hydrolysis of α-Triphenylmethylthioacetic Acid (Biilmann and Due, *Bull. Soc. chim.*, 1924, **35**, 368).—(*a*) The acid (2 g.) in alcohol (100 c.c.) was treated with concentrated hydrochloric acid (30 c.c.) and water (30 c.c.), and the mixture boiled for 2 hours. After dilution, extraction with ether, and washing with sodium hydrogen carbonate solution to remove unchanged acid, the ether afforded a viscous oily substance which solidified after treatment with few c.c. of alcohol. The solid separated from dilute alcohol in colourless needles of *ethyl α-triphenylmethylthioacetate*, m. p. 94° (Found : C, 76·3; H, 6·2; S, 8·9. $C_{23}H_{22}O_2S$ requires C, 76·2; H, 6·1; S, 8·8%). Hydrolysis of this ester with alcoholic sodium hydroxide solution gave the original acid.

(*b*) The acid (0·1 g.) was dissolved in concentrated sulphuric acid, and the solution set aside for 5 mins. Dilution with water liberated a colourless solid, m. p. 164° alone or mixed with triphenylcarbinol. The acid was recovered unchanged after 2 hours' boiling with 10% sodium hydroxide solution.

Acid Hydrolysis of β-Triphenylmethylthiopropionic Acid (Biilmann and Due, *loc. cit.*).—(*a*) The acid (2·5 g.) was boiled with aqueous alcoholic hydrogen chloride as above for 2 hours. After dilution, extraction with ether, and washing with sodium hydrogen carbonate solution, the ether contained a viscous oil which solidified after treatment with alcohol. The solid separated from alcohol in colourless needles, m. p. 94° alone or mixed with triphenylmethane. The alcoholic filtrate from the oil was shown to contain triphenylmethane and the ethyl ester of the original acid which were separated from each other by hydrolysis with alcoholic alkali.

(*b*) Hydrolysis with concentrated sulphuric acid as with above gave triphenylcarbinol, m. p. 164°. The acid was recovered unchanged after 2 hours' boiling with 10% sodium hydroxide solution.

α-Desylthioacetic acid, β-desylthiopropionic acid, α-(benzoylbenzhydrylthio)acetic acid, and β-(benzoylbenzhydrylthio)propionic acid were treated with aqueous-alcoholic hydrogen chloride as above for 2 hours. Little acid was recovered with sodium hydrogen carbonate, and the ether contained the oily ethyl esters which were hydrolysed with alcoholic sodium hydroxide in the cold to the corresponding starting acids. The benzoylbenzhydrylthio-acids on treatment with concentrated sulphuric acid as above gave a colourless solid, m. p. 136° alone or mixed with benzoyldiphenylmethane.

Acid Hydrolysis of Phenyl Triphenylmethyl Sulphide (Lecher, *Ber.*, 1915, **48**, 524).—(*a*) The substance was recovered unchanged from aqueous-alcoholic hydrogen chloride after long boiling. (*b*) The sulphide, on treatment with concentrated sulphuric acid as above gave triphenylcarbinol, and the filtrate was found to contain thiophenol (oxidised by iodine solution to diphenyl disulphide, m. p. 61°). The substance was recovered completely unchanged after boiling for 4 hours in alcoholic sodium hydroxide solution.

Acid Hydrolysis of Phenyl α-Benzoylbenzhydryl Sulphide (Schönberg and Iskander, *loc. cit.*).—(*a*) The substance was recovered unchanged from aqueous-alcoholic hydrogen chloride after long boiling. (*b*) Treatment of the substance with concentrated sulphuric acid as above gave benzoyldiphenylmethane, m. p. 136° (extracted with ether), and the mother-liquor contained thiophenol. Phenyl desyl sulphide (Schönberg and Iskander, *loc. cit.*) was also found to be very stable towards boiling aqueous-alcoholic hydrogen chloride, but extensively decomposed by concentrated sulphuric acid, giving a deep blue viscous mass with evolution of sulphur dioxide and the odour of thiophenol.

Neutral and Acid Hydrolysis of Didesyl Sulphide (Schönberg and Iskander, *loc. cit.*).—The form of m. p. 169° dissolved in boiling absolute alcohol without any change in colour, but after the addition of few drops of water the solution gradually became blue, but this faded and finally disappeared after 7 hours' boiling. Dilution with water and extraction with ether gave about half of the original substance, m. p. 169° (insoluble in the ether layer), and the ether contained the other form of didesyl sulphide, m. p. 129°, mixed with a yellow viscous substance which, after repeated fractional crystallisation from dilute alcohol, was found to be a mixture of benzil and deoxybenzoin. In presence of hydrochloric acid the same products were isolated. In concentrated sulphuric acid the substance dissolved in the cold with a faint blue colour which became dark blue in the course of ½ hour. On addition of water the blue colour disappeared, and the precipitated oily substance, which partly solidified after some time, was found to contain the original substance, m. p. 169°. The rest of the oil, extracted with ether, was found to be the other form, m. p. 129°. Desylthiol and α-benzoylbenzhydrylthiol dissolve in concentrated sulphuric acid without evolution of hydrogen sulphide, but triphenylmethylthiol liberates the gas in the cold (cf. Vorländer and Mittag, *loc. cit.*). A solution of desylthiol (1 g.) in concentrated sulphuric acid (10 c.c.) was left overnight; water was then added, and the liberated oil was extracted with ether. After evaporation of the ether, alcohol was added and precipitated some free sulphur, m. p. 118—120°. The alcohol-soluble part, after crystallisation from petroleum, proved to be deoxybenzoin.

FAROUK I UNIVERSITY,
FACULTY OF SCIENCE, ALEXANDRIA.

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