118. *The Reaction between Dibenzyl Disulphide and Sulphuryl Chloride.*

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The action of sulphuryl chloride on a simple disulphide, Ph·CH$_2$·S·S·CH$_2$Ph, has been investigated in order to provide by analogy an explanation of the action of sulphuryl chloride in imparting an unshrinkable finish to wool. In absence of water, the reaction follows a simple course, benzyl chloride and sulphur dioxide being the main products, although sulphur is liberated when the ratio of sulphuryl chloride to disulphide is not excessive. Fission of the same type may also occur in presence of water, but some disulphide is oxidised to the disulphoxide, which then undergoes fission in reaction with more sulphuryl chloride. In this case, therefore, the products include benzylsulphonyl chloride, as well as benzyl chloride and sulphur dioxide. Whether or not water is present, however, disulphide bond breakdown takes place, and it seems probable that sulphuryl chloride, like chlorine, renders wool unshrinkable by rupturing the cystine linkages between the peptide chains of the fibres. Support for this view is to be found in the fact that thionyl chloride, which is unsuitable for use in making wool unshrinkable, has no significant action on either dibenzyl disulphide or dibenzyl disulphoxide at low temperatures.

PRESENT-DAY methods of imparting an unshrinkable finish to wool depend for their success on the formation of a gelatinous degradation product of keratin on or under the surface scale structure of the fibres. As a rule, the necessary degradation is brought about by chlorine, the layer of cortex immediately underlying the scales being attacked preferentially when an aqueous solution of chlorine is used (Speakman and Goodings, *J. Text. Inst.*, 1926, **17**, T607). The attack may, however, be restricted to the surface of the fibres by taking advantage of the inaccessibility of dry fibres to reagents of comparatively low molecular weight (Speakman, *Trans. Faraday Soc.*, 1930, **26**, 61), as, for example, in the processes where gaseous chlorine (Wool Industries Research Association, King, and Galley, B.P. 417,719) or solutions of chlorine in inert organic solvents are applied to wool of low water content.

From first principles, it is evident that the degradation essential for unshrinkability must be realised by the fission of disulphide bonds or peptide linkages, the former being the more important. Apart from the fact that chlorine is known to cause disulphide bond breakdown (Zincke, *Ber.*, 1911, **44**, 769; *Annalen*, 1912, **391**, 55; Douglass and Johnson, *J. Amer. Chem. Soc.*, 1938, **60**, 1486), proof of this generalisation is afforded by the fact that chlorine peroxide, which converts cystine into cysteic acid (Schmidt and Braunsdorf, *Ber.*, 1922, **55**, 1529; Schmidt, Haag, and Sperling, *Ber.*, 1925, **58**, 1934), imparts an unshrinkable finish to wool when applied from solution in carbon tetrachloride. Further, since potassium permanganate, manganese heptoxide and Caro's acid can, under the correct conditions, be used to impart an unshrinkable finish to wool, it seems clear that any oxidising agent capable of causing disulphide bond breakdown is *ipso facto* a potential agent for producing unshrinkability (Speakman, Nilssen, and Elliott, *Nature*, 1938, **142**, 1035).

Hall (*J. Soc. Dyers and Col.*, 1939, **55**, 389; B.P. 464,503) has shown that wool is rendered unshrinkable by treatment with a solution of sulphuryl chloride in white spirit, but the cause of unshrinkability was not explained. By analogy with the behaviour of other reagents which serve the same purpose, however, it seemed probable that sulphuryl chloride would be found capable of causing disulphide bond breakdown. Its action on a simple disulphide was therefore investigated.* Although cystine, because of its presence in wool, may be regarded as the ideal disulphide for use in such experiments, dibenzyl disulphide was preferred on account of its ready solubility in organic solvents and its freedom from amino-groups. It has the further merit that the disulphide bond, as in cystine and wool, is situated between methylene groups.

According to Hall, the extent to which sulphuryl chloride minimises the felting power of wool depends to a marked extent on its water content: whereas wet wool is rendered unshrinkable by treatment with a 2·25% solution of sulphuryl chloride in white spirit for 1 hour at room temperature, dry wool is capable of marked shrinkage after similar treatment. It is not clear, however, whether the water, which seems to be essential for the success of the process, takes part in the reactions responsible for unshrinkability, or serves merely to swell the fibres and increase their accessibility to the reagent. In order to discriminate between these alternatives, the reaction between dibenzyl disulphide and sulphuryl chloride has been studied in presence and in absence of water.

The Reaction between Dibenzyl Disulphide and Sulphuryl Chloride in Presence of Water.—With undried ether (*d* 0·717) as the solvent, sulphuryl chloride was found to react slowly with dibenzyl disulphide at room temperature, but fairly complete reaction was realised in 1 hour at the temperature of boiling ether. Under these experimental conditions, the effect of varying the proportion of sulphuryl chloride was investigated. With one mol. of reagent (to one of disulphide), about half the disulphide was unchanged, and the remainder oxidised to dibenzyl disulphoxide. Although these features of the reaction are expressed by the equation:

$$\mathrm{Ph{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2Ph + 2SO_2Cl_2 \longrightarrow Ph{\cdot}CH_2{\cdot}SO_2{\cdot}S{\cdot}CH_2Ph + 2SOCl_2}$$

thionyl chloride could not be detected among the products. This first indication that sulphuryl chloride is not directly responsible for oxidation of the disulphide was afterwards confirmed by showing that the disulphoxide is not formed in absence of water. Even in presence of water, the disulphoxide was not isolated when higher ratios of sulphuryl chloride were used. With 2·1, 3·1, 4·0 and 5·6 mols., benzyl chloride was the main product of

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* Since the preparation of this paper, our attention has been drawn to the fact that Behaghel and Seibert (*Ber.*, 1933, **66**, 708) have utilised the reaction between sulphuryl chloride and aromatic diselenides to prepare arylselenium chlorides. In a footnote to the paper (p. 709) it is stated that arylsulphur chlorides can be made from aromatic disulphides in the same way.

reaction, but in the last case, 0·14 mol. of benzylsulphonyl chloride was also isolated. A still smaller amount of the sulphonyl chloride was obtained when 11·6 mols. of sulphuryl chloride were used.

If the first stage in the reaction between dibenzyl disulphide and sulphuryl chloride is the formation of dibenzyl disulphoxide, the latter should undergo fission in reaction with sulphuryl chloride to give benzyl chloride and benzylsulphonyl chloride, which are the compounds formed when dibenzyl disulphide is treated with excess of sulphuryl chloride. Although little reaction took place between dibenzyl disulphoxide and one mol. of sulphuryl chloride in 5 hours at 37°, 2·2 mols. gave a yield of 0·76 mol. of benzylsulphonyl chloride. As in the case of the disulphide, the use of a still higher ratio (3·2 mols.) resulted in a decrease in the yield of benzylsulphonyl chloride (0·63 mol.), benzyl chloride being a main product of reaction. Despite the general similarity of their behaviour, the disulphoxide differs from the disulphide in giving a greater yield of benzylsulphonyl chloride, suggesting that the disulphide may undergo fission without, as well as after, conversion into the disulphoxide. Support for this view is to be found in later experiments.

Although dibenzyldisulphone was not isolated in any of the preceding experiments, consideration was given to the possibility that it might be formed as an unstable intermediate. Attempts were made to synthesise the compound with a view to studying its behaviour in reaction with sulphuryl chloride. So far as we have been able to discover, no α-disulphones have been prepared with the sulphur atoms between methylene groups, but aryl α-disulphones have been synthesised by Kohler and MacDonald (*Amer. Chem. J.*, 1899, **22**, 219), using the reaction between a sodium arylsulphinate and an arylsulphonyl chloride; and by Hilditch (J., 1908, **93**, 1524), using the controlled oxidation of an arylsulphinic acid. Attempts to prepare dibenzyldisulphone by these methods met with complete failure, dibenzylsulphone and dibenzyl, respectively, being obtained. Dibenzylsulphone was also isolated during an attempt to prepare the disulphone by oxidation of the disulphoxide. Unlike aryl α-disulphones, therefore, dibenzyldisulphone appears to be unstable. Evidence that the formation of a disulphone is not an essential step in the reaction between disulphides and sulphuryl chloride was, however, obtained from experiments with di-*p*-tolyldisulphone, which is readily synthesised. Although the corresponding disulphide gave an appreciable quantity of *p*-chlorotoluene when refluxed for 1 hour with an ethereal solution of sulphuryl chloride (5·9 mols.), the disulphone was recovered unchanged after being heated for 3 hours at 58—60° with sulphuryl chloride (17·3 mols.) dissolved in benzene.

Finally, since benzyl chloride and benzylsulphonyl chloride are formed when either dibenzyl disulphide or dibenzyl disulphoxide is allowed to react with sulphuryl chloride, sulphur dioxide should be liberated. Its formation was demonstrated by carrying out the reactions in a stream of oxygen-free nitrogen, absorbing the volatile products in caustic soda solution, and titrating them against standard iodine solution. The amount of sulphur dioxide evolved was found to increase with the amount of sulphuryl chloride used, up to 7 mols. being liberated in the case of the disulphide, and 5·4 mols. with the disulphoxide. If benzyl chloride and sulphur dioxide are the ultimate products in both cases, the minimum theoretical yield of sulphur dioxide is 3 mols.—2 from the disulphide or disulphoxide and 1 from sulphuryl chloride—but higher yields are inevitable if the sulphuryl chloride acts, directly or indirectly, as an oxidising agent.

The Reaction between Dibenzyl Disulphide and Sulphuryl Chloride in Absence of Water.—In striking contrast with their behaviour in undried solvents, dibenzyl disulphide and sulphuryl chloride (1 mol.), after being heated together for 1 hour at 37—39° in sodium-dried ether or sodium-dried benzene, gave an oily product from which dibenzyl disulphoxide could not be isolated, even after the addition of water. Unlike arylsulphur chlorides, too, the oil did not react with acetophenone to give compounds of the type $R\cdot S\cdot CH_2\cdot COPh$ (Zincke, *Ber.*, 1911, **44**, 769). Either benzylsulphur chloride is not formed, or complex reactions succeed its formation, when dibenzyl disulphide reacts with sulphuryl chloride in absence of water, and it is obvious that water plays an essential part in the formation of dibenzyl disulphoxide when undried solvents are used. In confirmation of this deduction, the disulphoxide was again isolated when dibenzyl disulphide and sulphuryl chloride were allowed to react in presence of sodium-dried ether to which known amounts of water had been added. With 1 mol. of sulphuryl chloride, 0·16 and 0·24 mol. of dibenzyl disulphoxide were obtained in presence of 1 and 2 mols. of water, respectively.

When higher proportions of sulphuryl chloride (3·6 and 4·0 mols.) were allowed to react with the disulphide in dry benzene at 37—39° for 3 hours, both free sulphur and benzyl chloride were isolated, suggesting that one of the reactions between dibenzyl disulphide and sulphuryl chloride, in absence of water, is as follows :

$$\mathrm{Ph{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2Ph + SO_2Cl_2 \longrightarrow 2Ph{\cdot}CH_2Cl + SO_2 + 2S}$$

By carrying out the reaction in a stream of oxygen-free nitrogen, the amount of sulphur dioxide evolved, when 2·5 mols. of sulphuryl chloride were used, was found to be 1·24 mols. Benzyl chloride was the main product with still greater amounts of sulphuryl chloride (7·5 and 11·0 mols.), but free sulphur could not be detected.

Although dibenzyl disulphoxide is not formed when dibenzyl disulphide reacts with sulphuryl chloride in absence of water, the behaviour of the disulphoxide with sulphuryl chloride in dry benzene was examined. 6·3 Mols. of sulphuryl chloride being used, 0·9 mol. of benzyl chloride was obtained after 1 hour's reaction at 37—39°.

The Reaction between Dibenzyl Disulphide and Thionyl Chloride in Presence of Water.— Unlike sulphuryl chloride, thionyl chloride is unsuitable for use in imparting an unshrinkable finish to wool, and if the earlier argument concerning the cause of unshrinkability is correct, thionyl chloride should be incapable of causing disulphide bond breakdown.

Undried ether, or dry ether to which a known amount of water had been added, being used, thionyl chloride (1·0, 5·2, and 10·4 mols.) was found to be without significant action on dibenzyl disulphide in 1—3 hours at 37—39°. Similarly, it was without effect on dibenzyl disulphoxide under similar conditions. In certain of the experiments with both the disulphide and the disulphoxide, the volatile products were carried over into caustic soda solution in a stream of oxygen-free nitrogen, and determinations of chlorine and sulphur dioxide showed that almost all the thionyl chloride was unaltered at the end of the reaction period.

DISCUSSION.

When benzylthiol is treated with chlorine in presence of water (Douglass and Johnson, *loc. cit.*), the products include dibenzyl disulphide, dibenzyl disulphoxide and benzylsulphonyl chloride. Similarly, when sulphuryl chloride reacts with dibenzyl disulphide in presence of water, dibenzyl disulphoxide and benzylsulphonyl chloride are formed, although benzyl chloride is the chief ultimate product. This similarity between chlorine and sulphuryl chloride, as regards their attack on a simple disulphide, is such as to suggest that sulphuryl chloride acts simply as a source of chlorine, which oxidises the disulphide to the disulphoxide in presence of water. Direct oxidation may not take place, and the following alternative scheme is based on the work of Otto (*Ber.*, 1886, **19**, 1235) and v. Braun and Weissbach (*Ber.*, 1930, **63**, 2836) :

$$\mathrm{Ph{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2Ph + SO_2Cl_2 \longrightarrow 2Ph{\cdot}CH_2{\cdot}SCl + SO_2}$$

In presence of water, the sulphur chloride is hydrolysed :

$$\mathrm{2Ph{\cdot}CH_2{\cdot}SCl + 2H_2O \longrightarrow 2Ph{\cdot}CH_2{\cdot}S{\cdot}OH + 2HCl}$$

and the sulphenic acid is converted into benzylthiol and the sulphinic acid :

$$\mathrm{2Ph{\cdot}CH_2{\cdot}S{\cdot}OH \longrightarrow Ph{\cdot}CH_2{\cdot}SH + Ph{\cdot}CH_2{\cdot}SO_2H}$$

These products would react with more sulphenic acid to give dibenzyl disulphide and dibenzyl disulphoxide, respectively, and the complete reaction may be summarised in the equation :

$$\begin{aligned}\mathrm{2Ph{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2Ph + 2SO_2Cl_2 + 4H_2O} &\longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2Ph +} \\ &\mathrm{Ph{\cdot}CH_2{\cdot}SO_2{\cdot}S{\cdot}CH_2Ph + 2H_2O + 4HCl + 2SO_2}\end{aligned}$$

Left in this form, the equation indicates that, in agreement with the experimental findings, half the disulphide remains unchanged and the remainder is oxidised to the disulphoxide with evolution of sulphur dioxide, when dibenzyl disulphide reacts with an equimolecular proportion of sulphuryl chloride in presence of water. The above scheme has the further merit of indicating why dibenzyl disulphoxide is not formed when the disulphide is treated with sulphuryl chloride in absence of water.

Since the disulphoxide gives benzyl chloride and benzylsulphonyl chloride in reaction with sulphuryl chloride, the further course of the reaction may be written :

$$Ph{\cdot}CH_2{\cdot}SO_2{\cdot}S{\cdot}CH_2Ph + SO_2Cl_2 \longrightarrow Ph{\cdot}CH_2{\cdot}SO_2Cl + Ph{\cdot}CH_2Cl + S + SO_2$$

The formation of dibenzyl disulphoxide is not, however, an essential preliminary to disulphide bond breakdown. When the disulphide is treated with sulphuryl chloride in absence of water, the main products are benzyl chloride and sulphur dioxide, despite the fact that dibenzyl disulphoxide is not formed. Since sulphur is also liberated when the amount of sulphuryl chloride is not excessive, the second type of reaction which the disulphide can undergo may be written :

$$Ph{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2Ph + SO_2Cl_2 \longrightarrow 2Ph{\cdot}CH_2Cl + SO_2 + 2S$$

Except under conditions of absolute dryness, both the above types of reaction will proceed side by side, the first being favoured by the presence of water and a low ratio of sulphuryl chloride; the second by absence of water and a high ratio of sulphuryl chloride.

Although the reaction follows different courses in presence and in absence of water, the main end-products are the same in both cases. In practice, however, the presence of water in wool facilitates the action of sulphuryl chloride in promoting unshrinkability. Disulphide bond breakdown may, of course, proceed more rapidly when there is intermediate formation of the disulphoxide, but it seems likely that water facilitates the action of sulphuryl chloride by swelling the fibres and making them more accessible to the reagent.

Indirect support for the view that sulphuryl chloride, like chlorine, promotes unshrinkability by causing disulphide bond breakdown is afforded by the fact that thionyl chloride, which is unsuitable for use in making wool unshrinkable, has no action on dibenzyl disulphide and dibenzyl disulphoxide at low temperatures.

EXPERIMENTAL.

(a) *Preparation of Materials.*—Dibenzyl disulphide (m. p. 72°), prepared by the method of Price and Twiss (J., 1909, **95**, 1489; 1914, **105**, 1140), was oxidised with hydrogen peroxide (Smythe, J., 1912, **101**, 2076) to dibenzyl disulphoxide (m. p. 108°). Benzylsulphonyl chloride (m. p. 93°) was prepared by a slight modification of Limpricht's method (*Ber.*, 1873, **6**, 534).

*Di-*p*-tolyl disulphide.* *p*-Tolylthiol was dissolved in the theoretical amount of N-sodium hydroxide and treated at room temperature with a 5% excess of hydrogen peroxide. The disulphide (yield, 85%) had m. p. 45° after recrystallisation from alcohol.

*Di-*p*-tolyldisulphone.* *p*-Toluenesulphinic acid (Bloomstrand, *Ber.*, 1870, **3**, 965) was treated with an equivalent quantity of *p*-toluenesulphonyl chloride under the conditions described by Kohler and MacDonald (*loc. cit.*). The crude disulphone (yield, 55%; m. p. 202—206°) was recrystallised from benzene and gave rhombic crystals, m. p. 221—222°.

Action of Sulphuryl Chloride on Dibenzyl Disulphide in Presence of Water.—(i) Dibenzyl disulphide (4·92 g.) was dissolved in undried ether (100 c.c.), sulphuryl chloride (2·7 g.; 1·0 mol.) added, the ether removed in a vacuum after 1 hour and water added to the residue. The bulk of the organic material crystallised after 1 hour, giving 4·14 g., m. p. 62—64°, and a further 0·76 g., m. p. 57—61°. Mixed m. p. determinations showed that these products were impure disulphide.

(ii) A mixture of dibenzyl disulphide (6·32 g.), sulphuryl chloride (3·5 g.; 1·0 mol.), and undried ether (100 c.c.) was boiled under reflux for 1 hour. Afterwards, 75% of the ether was allowed to boil away, and the crystals (2·79 g., m. p. 104—105°) which separated were filtered off. The filtrate was again concentrated, but the solid which then separated (3·66 g., m. p. 65—66°) was impure disulphide. Under similar conditions, a second experiment with dibenzyl disulphide (6·04 g.) and sulphuryl chloride (3·6 g.; 1·1 mols.) gave 3·92 g. of a product, m. p. 97—100°, and 2·45 g. of impure disulphide, m. p. 65—67°. In a third experiment, dibenzyl disulphide (2·00 g.) and sulphuryl chloride (1·3 g.; 1·2 mols.) were dissolved in undried benzene

(40 c.c.) and heated for 1 hour at 37—39°. The benzene was then evaporated in a stream of nitrogen at the same temperature, and the product was separated by the addition of ether into 0·84 g., m. p. 92—97°, and 1·49 g. of an oily solid, which smelt of benzyl chloride. After being drained on a porous tile, 0·76 g. of impure disulphide (m. p. 57—60°) was recovered.

The fraction of higher m. p. in each of the preceding experiments was found to be dibenzyl disulphoxide, m. p. 108° after recrystallisation from benzene–light petroleum, not depressed by authentic material (Found : C, 60·5; H, 4·8; S, 23·3. Calc. : C, 60·4; H, 5·0; S, 23·0%).

A fourth experiment was carried out to discover whether thionyl chloride is formed during the oxidation of the disulphide to the disulphoxide. Dibenzyl disulphide (11·40 g.), sulphuryl chloride (6·3 g.; 1·0 mol.), and sodium-dried ether (60 c.c.) to which water (0·85 g.; 1 mol.) had been added, were heated at 37—39° for 1 hour, the liquid then being evaporated under reduced pressure (15 mm.) *via* a small tube of phosphoric oxide. The distillation products were collected in a small flask cooled by solid carbon dioxide–acetone, and then fractionated slowly until 4—5 c.c. remained. On treatment with *p*-phenylenediamine hydrochloride (Michaelis, *Ber.*, 1893, **26**, 2192; *Annalen*, 1893, **274**, 250), followed by filtration and evaporation, this residue did not give the golden-yellow needles, m.p. 115°, obtained in experiments with *p*-phenylenediamine and thionyl chloride. In fact, nothing remained after evaporation, showing that *thionyl chloride was not formed.* Similar results were obtained in an experiment with dry benzene as the solvent.

(iii) Dibenzyl disulphide (1·00 g.), sulphuryl chloride (1·1 g.; 2·1 mols.), and undried ether (50 c.c.) were boiled under reflux for 1 hour. The solution was concentrated to 10 c.c. and exposed to caustic soda in a vacuum, but crystallisation did not occur. The product was a pale yellow oil (1·09 g.) with a strong smell of benzyl chloride.

(iv) Dibenzyl disulphide (7·11 g.), sulphuryl chloride (12·1 g.; 3·1 mols.), and undried ether (50 c.c.) were refluxed for 1 hour. The subsequent procedure was exactly as under (iii) and 8·47 g. of a yellow oil, smelling strongly of benzyl chloride, were obtained. The oil deposited a little solid on standing.

(v) Dibenzyl disulphide (6·04 g.), sulphuryl chloride (13·2 g.; 4·0 mols.), and undried ether (100 c.c.) were refluxed for 1 hour. After evaporation of the ether, water was added. One hour later, the organic product was extracted with ether, and the ethereal solution was washed with water and sodium bicarbonate solution before being dried over anhydrous sodium sulphate. Ether was then removed by evaporation; the product (7·15 g.) gave on distillation a colourless oil (3·2 g., b. p. 180°) which resembled benzyl chloride. Some sulphur dioxide was evolved during distillation. The oily distillate contained carbon, hydrogen, and chlorine, and was identified as benzyl chloride by oxidation to benzoic acid (m. p. 120°) with potassium permanganate, as well as by the preparation of benzyl 3 : 5-dinitrobenzoate (m. p. 113°).

(vi) Dibenzyl disulphide (6·04 g.) and sulphuryl chloride (18·5 g.; 5·6 mols.) were refluxed with undried ether for 1 hour, and then treated in exactly the same manner as under (v), except that the oil obtained by concentrating the dry ethereal extract was not distilled. Colourless, crystalline plates separated on standing (0·66 g.), leaving an oil (5·58 g.) which was mainly benzyl chloride. The crystals contained carbon, hydrogen, chlorine and sulphur, decomposed on heating to form sulphur dioxide and benzyl chloride, and were identical with benzylsulphonyl chloride, m. p. 93°. Benzylsulphonamide prepared from the crystals was identical with authentic material, m. p. 102°.

(vii) Dibenzyl disulphide (2·35 g.), sulphuryl chloride (15·0 g.; 11·6 mols.), and undried ether (60 c.c.) were refluxed for 1 hour, the liquid then being concentrated to 10 c.c. The product was washed with dilute sodium carbonate solution, taken up in ether, dried over anhydrous sodium sulphate, and then freed from ether by evaporation. With a view to estimating the amount of benzylsulphonyl chloride in the product, it was heated in a stream of oxygen-free nitrogen for 90 minutes at 150—160°. The nitrogen stream was maintained during subsequent cooling (30 minutes) and the sulphur dioxide formed by decomposition of the sulphonyl chloride was thus carried into a wash-bottle containing excess of N/5-iodine, which was subsequently back-titrated with N/10-sodium thiosulphate. Blank experiments with benzylsulphonyl chloride showed that under the above conditions, 98·6% of the theoretical amount of sulphur dioxide is evolved and estimated. In the case under consideration, the amount of sulphur dioxide evolved from the product was only 0·025 mol. (per mol. of disulphide), so the product was almost entirely benzyl chloride.

Action of Sulphuryl Chloride on Dibenzyl Disulphoxide in Presence of Water.—(i) Dibenzyl disulphoxide (1·00 g.), sulphuryl chloride (0·60 g.; 1·2 mols.), and undried ether (60 c.c.) were refluxed for 5 hours, and the volume then reduced to 10 c.c. by evaporation. After exposure to caustic soda in a vacuum, the product (1·10 g.), which contained a trace of benzyl chloride, was drained on a porous tile and gave 0·97 g. of crystals, m. p. 104—106°.

Dibenzyl disulphoxide (0·85 g.), sulphuryl chloride (0·44 g.; 1·1 mols.), and undried benzene (40 c.c.) were heated at 37—39° for 2 hours and then for 8 hours in a stream of nitrogen. After exposure to caustic soda in a vacuum, the product weighed 0·84 g., m. p. 97—104°.

(ii) Dibenzyl disulphoxide (0·94 g.), sulphuryl chloride (1·0 g.; 2·2 mols.), and undried benzene (40 c.c.) were maintained at 37—39° for 1 hour and then during evaporation in a stream of nitrogen (12 hours). During exposure to caustic soda in a vacuum, the product (1·07 g.) crystallised and was separated into two parts by trituration with three lots of 0·4 c.c. of light petroleum. A solid fraction (0·57 g.), m.p. 70—77° (mixed m. p. with benzylsulphonyl chloride 74—80°), and a liquid fraction (0·35 g.) were obtained. When portions of these two fractions were analysed by the method already described (p. 646), the total original reaction product was found to contain 0·49 g. (0·76 mol.) of benzylsulphonyl chloride. The remainder (0·58 g.) was a mixture of benzyl chloride and dibenzyl disulphoxide.

(iii) Dibenzyl disulphoxide (1·16 g.), sulphuryl chloride (1·8 g.; 3·2 mols.), and undried ether (50 c.c.) were boiled under reflux for 1 hour. After removal of most of the ether, the residue was exposed to caustic soda in a vacuum. Crystallisation took place and the product (1·45 g.) was separated into two parts by means of 0·5 c.c. of petrol. The crystals were drained on a tile (0·37 g.), and the solution evaporated to give an oil (0·83 g.). Under similar conditions, a blank experiment with 0·59 g. of benzylsulphonyl chloride and 0·88 g. of benzyl chloride gave 0·44 g. of crystals and 0·65 g. of oil. The amount of benzylsulphonyl chloride in the reaction product was thus no more than 0·5 g. or 0·63 mol. (per mol. of disulphoxide).

Action of Sulphuryl Chloride on Di-p-tolyl Disulphide in Presence of Water.—(i) Di-*p*-tolyl disulphide (1·66 g.), sulphuryl chloride (5·3 g.; 5·9 mols.), and undried ether (60 c.c.) were boiled under reflux for 1 hour. After removal of most of the ether, the product was exposed to caustic soda in a vacuum. A crystalline sublimate (0·18 g., m. p. 35—37°) of disulphide was formed and an orange oil (1·94 g.) remained. The latter gave on distillation 0·42 g., b. p. 150—160°, and a second fraction, b. p. 220—240°, which was the disulphide, but there was a considerable residue. When it was oxidised with a mixture of chromic acid and sulphuric acid, *p*-chlorobenzoic acid was obtained from the first fraction, which consisted mainly of *p*-chlorotoluene.

Action of Sulphuryl Chloride on Di-p-tolyldisulphone in Presence of Water.—(i) Di-*p*-tolyldisulphone (1·00 g.), sulphuryl chloride (6·7 g.; 17·3 mols.), and undried benzene were heated at 58—60° for 3 hours. After the product had been exposed to caustic soda in a vacuum, unchanged disulphone remained (1·02 g., m. p. 216—218°).

Evolution of Sulphur Dioxide in the Reaction between Sulphuryl Chloride and Dibenzyl Disulphide or Dibenzyl Disulphoxide in Presence of Water.—The disulphide or disulphoxide (0·2—1·3 g.) was weighed out into a 20 c.c. distilling flask, undried benzene (10 c.c.) added, and the required amount of sulphuryl chloride introduced (0·26—1·00 c.c.). The sulphuryl chloride was contained in a small glass tube, and was not allowed to come into contact with the disulphide until the apparatus had been freed from air by a stream of nitrogen, which had been purified by passage through (i) alkaline potassium permanganate, (ii) alkaline pyrogallol, (iii) a tube containing granular copper and copper gauze at a temperature just below red heat, and (iv) a long column of anhydrous calcium chloride. During the reaction, the flask was kept in a water bath at 37—39°, and the nitrogen stream was almost stopped for about 3 hours. Thereafter, the stream of nitrogen was increased and maintained for 18 hours. Sealed to the delivery tube of the distilling flask was a train of two wash-bottles, one containing 40 c.c. of 10% sodium hydroxide solution and the other 40 c.c. of 5% sodium hydroxide solution, which had been made up with air-free distilled water. After addition of alcohol as antioxidant, the sulphite content of these solutions was estimated by titration against standard iodine solution acidified with hydrochloric acid. The results are in Table I.

TABLE I.

	Moles per mole of dibenzyl disulphide.						
Sulphuryl chloride taken	1·00	1·53	2·94	4·38	5·77	8·25	13·26
Sulphite	0·71	1·27	2·75	4·37	5·46	6·49	6·96
	Moles per mole of dibenzyl disulphoxide.						
Sulphuryl chloride taken	1·10	1·68	2·60	4·09	7·25	10·57	
Sulphite	1·36	1·99	2·94	3·64	4·64	5·35	

Action of Sulphuryl Chloride on Dibenzyl Disulphide in Absence of Water.—(i) Dibenzyl disulphide (6·51 g.), sulphuryl chloride (3·6 g.; 1·0 mol.), and sodium-dried ether (100 c.c.)

were heated at 37—39° for 1 hour in an atmosphere of dry nitrogen, and the liquid then evaporated in a stream of nitrogen. The product, after exposure to caustic soda in a vacuum, was a sticky yellow oil, which deposited a little disulphide on standing.

The experiment was repeated with dibenzyl disulphide (1·98 g.), sulphuryl chloride (1·1 g.; 1·0 mol.), and sodium-dried ether (40 c.c.), except that the oily reaction product was afterwards treated with 10 c.c. of dry ether to which 0·28 g. (2 mols.) of water had been added. Crystallisation did not take place.

Dibenzyl disulphide (3·30 g.), sulphuryl chloride (1·8 g.; 1·0 mol.), and sodium-dried benzene (40 c.c.) were allowed to react under the above conditions. The solution was concentrated by evaporation under reduced pressure, and a little dry ether added, but crystals did not separate. Water (0·48 g.; 2 mols.) was added, but without visible effect, even after 24 hours.

Dibenzyl disulphide (2·33 g.), sulphuryl chloride (1·3 g.; 1·0 mol.), and sodium-dried benzene (40 c.c.) were heated for 1 hour in an atmosphere of dry nitrogen, and the liquid then evaporated in a stream of nitrogen. After being exposed to caustic soda in a vacuum, the product was treated with acetophenone (2·27 g.; 2·0 mols.) in chloroform (10 c.c.). On heating, a very small quantity of hydrogen chloride was evolved, but no crystals were obtained. Conversion into the semicarbazone gave the derivative of acetophenone substantially pure, and an oil which deposited a little impure disulphide.

Dibenzyl disulphide (1·92 g.), sulphuryl chloride (1·1 g.; 1·0 mol.), and dry ether (40 c.c.), to which water * (0·28 g.; 2·0 mol.) had been added, were boiled under reflux for 1 hour. Afterwards, 75% of the ether was allowed to boil away; crystals (1·07 g., m. p. 62—70°) separated. When the filtrate from these crystals was again concentrated, a further 0·91 g., m. p. 60—65°, was obtained. After trituration with ether (25 c.c.) the first product gave 0·34 g. of crude dibenzyl disulphoxide, m. p. 95—101°.

The preceding experiment was repeated with dibenzyl disulphide (3·26 g.), sulphuryl chloride (1·8 g.; 1·0 mol.), and dry ether (40 c.c.), to which water * (0·24 g.; 1·0 mol.) had been added. Crude dibenzyl disulphoxide (0·88 g., m. p. 99—102°) and a product (1·44 g.) melting indefinitely at 40° were obtained, but some oil and benzyl chloride were present.

(ii) Dibenzyl disulphide (1·37 g.), sulphuryl chloride (3·0 g.; 4·0 mols.), and dry benzene (40 c.c.) were heated at 37—39° for 3 hours in an atmosphere of dry nitrogen, and the liquid then evaporated in a stream of nitrogen. The product was exposed to caustic soda in a vacuum; rhombic crystals (0·067 g., m. p. 115—117°) separated. After recrystallisation from benzene, the product (m. p. 120°) gave S, 100%.

The experiment was repeated with dibenzyl disulphide (8·93 g.), sulphuryl chloride (17·1 g.; 3·6 mols.), and dry benzene (80 c.c.). After removal of the sulphur (0·162 g.) which separated from the product, the liquid portion was dissolved in ether, shaken with sodium bicarbonate solution, and dried over anhydrous potassium carbonate. The product obtained on evaporation (6·85 g.) was shown to contain benzyl chloride by treatment with silver 3 : 5 dinitrobenzoate (16·5 g.) in alcohol. Crude benzyl 3 : 5 dinitrobenzoate (7·32 g., m. p. 108—111°) was obtained, the m. p. and mixed m. p. being 113° after crystallisation from aqueous alcohol.

(iii) Dibenzyl disulphide (2·27 g.), sulphuryl chloride (9·3 g.; 7·5 mols.), and dry benzene (40 c.c.) were heated together in an atmosphere of dry nitrogen as in the preceding experiments. No sulphur could be isolated from the product.

(iv) Dibenzyl disulphide (1·05 g.), sulphuryl chloride (6·3 g.; 11·0 mols.), and dry benzene (10 c.c.) were heated for 1 hour at 37—39° in an atmosphere of nitrogen. Sulphur did not separate from the residue which remained after evaporation, and distillation gave benzyl chloride (0·85 g., b. p. 179—183°).

Evolution of Sulphur Dioxide in the Reaction between Sulphuryl Chloride and Dibenzyl Disulphide in Absence of Water.—Dibenzyl disulphide (0·90 g.), sulphuryl chloride (1·3 g.; 2·5 mols.), and dry benzene (10 c.c.) were heated in an atmosphere of nitrogen for 3 hours at 37—39°. As before, the volatile products were carried over into caustic soda solution in a stream of nitrogen, which was maintained for 18 hours. After alcohol (10 c.c.) had been added and the volume made up to 250 c.c. with water, 100 c.c. of the alkaline solution were removed and titrated against standard iodine solution acidified with hydrochloric acid. The reducing agent present being assumed to be sodium sulphite, the sulphur dioxide liberated during the reaction was found to be 1·24 mols. To prove that no other reducing agent was present, a

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* Although water was added, this experiment is included here for convenient comparison with corresponding experiments in absence of water, and to maintain a strict parallel between the general and the experimental section of the paper.

second lot of 100 c.c. was acidified with sulphuric acid and then heated to 70° in a stream of nitrogen. The nitrogen was again bubbled through caustic soda solution, and titration of an aliquot showed that 1·23 mols. of sulphur dioxide were recovered. Further, when the solution was acidified, the presence of sulphur dioxide was recognised by its smell and bleaching properties.

Action of Sulphuryl Chloride on Dibenzyl Disulphoxide in Absence of Water.—(i) Dibenzyl disulphoxide (1·04 g.), sulphuryl chloride (3·2 g.; 6·3 mols.), and dry benzene (10 c.c.) were heated in an atmosphere of nitrogen for 1 hour at 37—39°, and the liquid then evaporated in a stream of nitrogen. When the residue was distilled, 0·43 g. or 0·91 mol. of benzyl chloride, b. p. 175—183°, was obtained. There was a substantial black residue.

Action of Thionyl Chloride on Dibenzyl Disulphide in Presence of Water.—(i) Dibenzyl disulphide (1·97 g.), thionyl chloride (1·0 g.; 1·0 mol.), and dry ether (40 c.c.), to which water (0·14 g.; 1·0 mol.) had been added, were heated for 1 hour at 37°, and the whole evaporated under reduced pressure and then exposed to caustic soda in a vacuum. The product (1·96 g.) was unchanged disulphide, m. p. 69—71°.

(ii) Dibenzyl disulphide (4·00 g.), thionyl chloride (10·0 g.; 5·2 mols.), and undried ether (100 c.c.) were refluxed for 1 hour, the ether being then removed by evaporation at 40—60°. After the residue had been treated with water, the crystalline solid was filtered off, washed with dilute sodium carbonate solution and water, and dried in a vacuum. When recrystallised from ethanol, the product (originally 4·08 g., m. p. 62—64°) gave 3·04 g., m. p. 72°, not depressed by dibenzyl disulphide.

(iii) Dibenzyl disulphide (1·31 g.), thionyl chloride (7·0 g.; 10·4 mols.), and undried ether (50 c.c.) were heated under reflux for 3 hours. The crude product, isolated under the same conditions as above, had the same weight as the original material and melted at 57—65°.

Action of Thionyl Chloride on Dibenzyl Disulphoxide in Presence of Water.—(i) Dibenzyl disulphoxide (0·73 g.), thionyl chloride (0·3 g.; 1·0 mol.), and dry ether (40 c.c.), to which water (0·05 g.; 1·0 mol.) had been added, were heated at 37° for 1 hour, and the whole evaporated under reduced pressure and then exposed to caustic soda in a vacuum. The product (0·73 g.) was unchanged disulphoxide, m. p. 104—107°.

(ii) Dibenzyl disulphoxide (1·02 g.), thionyl chloride (1·5 g.; 3·1 mols.), and undried ether (50 c.c.) were boiled under reflux for 2 hours. Most of the ether was then evaporated, and after exposure to caustic soda in a vacuum, the residue (1·07 g.) was unchanged disulphoxide, m. p. 106—107°.

Recovery of Thionyl Chloride after Heating with Dibenzyl Disulphide and Dibenzyl Disulphoxide in Benzene.—The experiments were carried out under the conditions described on p. 647, but the caustic soda solution was analysed for chlorine, sulphite, and, after oxidation with hydrogen peroxide, sulphate. The results (Table II) indicate that thionyl chloride is without significant action on either the disulphide or the disulphoxide at 37—39°.

TABLE II.

Thionyl chloride taken.	Sulphite.	Chloride (Cl_2).	Sulphate.
	Moles per mole of dibenzyl disulphide.		
5·57	5·28	5·31	5·34
	Moles per mole of dibenzyl disulphoxide.		
5·98	5·80	5·72	5·79

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