XLV.—*Benzyl Sulphoxide: a Possible Example of Dynamic Isomerism.*

By JOHN ARMSTRONG SMYTHE.

THE ease with which mercaptans condense with ketones suggests that similar reactions may take place between the mercaptans and the structural analogues of the ketones, namely, the sulphoxides. The attempt to condense together benzyl mercaptan and benzyl sulphoxide led to the detailed investigation of the latter which forms the main subject-matter of this communication. In the preliminary experiments both benzyl sulphide and benzyl disulphide were identified among the products of reaction, so that it seemed at first that the mercaptan and sulphoxide had reacted, not, indeed, to furnish the expected mercaptal, but its proximate substituents, thus :

Further study of the reaction showed, however, that the disulphide was greatly in excess of the sulphide, whence it was apparent that if the above reaction had taken place, it had done so to a relatively small extent ; and the control experiments proved that the condensing

agent, hydrochloric acid, has a specific action on the mercaptan and the sulphoxide, which, in the latter case, results in the formation of benzyl disulphide and sulphide. The action of hydrochloric acid on benzyl mercaptan is still under investigation; its action on benzyl sulphoxide will now be considered in detail.

One of the most striking features of this reaction is the extreme ease with which it takes place. If dry hydrogen chloride, for instance, is led on to the surface of dry benzyl sulphoxide, immediate action sets in, heat being evolved, and the mass becoming pasty from the formation of benzaldehyde and benzyl chloride. When the sulphoxide is dissolved in a solvent, it suffices to saturate this at the ordinary temperature to complete the decomposition. For reasons which will become apparent later, this reaction has been studied under a variety of conditions and in many different solvents, and an attempt has been made to estimate the products quantitatively. The method of working adopted is as follows :

The Action of Hydrochloric Acid on Benzyl Sulphoxide.

1. *Method.*—A weighed quantity of pure benzyl sulphoxide (m. p. 133°) is dissolved, or partly so, in four to ten times its weight of solvent, and dry hydrogen chloride passed in until the liquid is completely saturated. The reaction is carried out sometimes at the ordinary temperature, at other times on the water-bath, a suitable condensing arrangement being used in the latter case, and the passing of the gas into the liquid being continued during the cooling stage. In the earlier experiments, special efforts were made to trap volatile compounds, such as sulphur chloride, which might possibly be formed in the reaction, but such were not detected, and the quantitative data prove that they are not formed in appreciable quantity.

As soon as saturation is reached, the reaction is complete. On distilling in a current of steam, excess of the solvent passes over first, and then an oil heavier than water; the residue is cooled and agitated to granulate the solid.

The *distillate* is extracted with ether (where acetic acid has been used it is advisable to neutralise this before extraction), the ethereal solution dried, and the ether evaporated. The residual oil, despite its constant boiling point (179°), is a mixture of benzyl chloride and benzaldehyde, sometimes containing a little mercaptan. The method used to separate these quantitatively is to shake the ethereal solution with a strong, freshly-prepared solution of sodium hydrogen sulphite. After keeping for several hours, with frequent shakings, the crystals of the hydrogen sulphite compound are collected, washed with ether, then dried on a porous plate, and weighed. Distillation of these with

sodium carbonate in a current of steam yields the free aldehyde, which can be collected and weighed, when in sufficient quantity, as a check on the bisulphite determination. The ethereal liquors from the hydrogen sulphite compound are then dried and distilled from a tared flask, and the weight of the benzyl chloride is determined after all the ether has been expelled. The identity of the benzyl chloride is then fixed by a determination of its boiling point. When benzyl mercaptan is present, it can be estimated, after removal of the aldehyde and ether, by shaking the residual oil with standard iodine solution.

The *residue* from the original steam distillation is ground with water, filtered, and weighed when dry. It is then submitted to an exhaustive process of fractional crystallisation. It may contain two or three of the following compounds, namely, benzyl sulphide, benzyl disulphide, benzyl disulphoxide, and benzaldehyde-benzylmercaptan. The isolation of these compounds in a pure state presents no special difficulties, but the attempt to estimate them quantitatively proved very laborious, for they do not differ markedly in solubility in the various solvents used, and a certain amount of loss was inevitable in the manipulation of sometimes more than fifty crops of crystals and as many mother liquors, and in the melting-point determinations of these crops. By careful working, however, the loss may be reduced to a low figure, and, omitting three of the earlier experiments made when the necessary skill had not been acquired, the average loss of solid products in nine reactions was only about 9 per cent. Alcohol was the chief solvent used, generally alone, but sometimes in admixture with ether and chloroform. Ethyl acetate and glacial acetic acid rendered good service in some cases, and small quantities of cold ether were found especially valuable in the separation of the disulphide from the disulphoxide. Cooling by ice or a freezing mixture was also advantageous in the treatment of residual liquors, which sometimes tend to become oily, and are readily soluble in ether, but not in other solvents.

From the above description it will readily be understood that exact quantitative data of this reaction are not attainable; results of considerable value, however, for a correct understanding of the reaction can be obtained, and duplicate determinations agree fairly satisfactorily with a maximum deviation of, say, one constituent of about 3 per cent.

2. *Identification of the Products of Reaction.*—As most of the substances mentioned are well known, organic analysis was used but sparingly for the purposes of identification. It may be convenient to bring together now such analyses as were made, and also to summarise the chief properties of the compounds which, along with odour, crystalline habit, etc., served as a means of identification throughout the whole course of the work. In the case of the solid compounds,

the determination of melting points of samples mixed with standard preparations was often resorted to as a check.

Benzyl chloride, b. p. 179° , yields with alcoholic sodium sulphide an oil with an odour of benzyl mercaptan, benzyl sulphide (m. p. 49°), and sodium chloride; oxidised by potassium permanganate to benzoic acid.

Benzyl mercaptan, $C_6H_5 \cdot CH_2 \cdot SH$, b. p. 195° , decolorises iodine solution, being oxidised to benzyl disulphide (m. p. 71°).

Benzyl sulphide, $(C_6H_5 \cdot CH_2)_2S$, m. p. 49° , is oxidised by nitric acid to benzyl sulphoxide, m. p. 133° . Of the following analyses, I and III are from samples prepared when acetic acid was the solvent; II, when chloroform was the solvent. (For analyses I, II, IV, V, VIII, I am greatly indebted to Mr. H. Blair, F.C.S.):

I. 0.1148 gave 0.3322 CO_2 and 0.0675 H_2O . C = 78.92; H = 6.53.

II. 0.1275 „ 0.3681 CO_2 „ 0.0794 H_2O . C = 78.71; H = 6.92.

III. 0.1764 „ 0.1913 $BaSO_4$. S = 14.86.

$C_{14}H_{14}S$ requires C = 78.50; H = 6.54; S = 14.95 per cent.

Benzyl disulphide, $(C_6H_5 \cdot CH_2)_2S_2$, m. p. 71° . When a cold alcoholic solution of this compound is mixed with one of silver nitrate, crystals of a double compound appear in the liquid, and develop without motion in spherical form until the whole liquid becomes filled with solid matter.

Analyses:—IV and VI from samples prepared in acetic acid solution; V, in alcoholic solution:

IV. 0.1313 gave 0.3280 CO_2 and 0.0674 H_2O . C = 68.13; H = 5.70.

V. 0.3610 „ 0.9021 CO_2 „ 0.1861 H_2O . C = 68.14; H = 5.73.

VI. 0.2340 „ 0.4460 $BaSO_4$. S = 26.18.

$C_{14}H_{14}S_2$ requires C = 68.30; H = 5.69; S = 26.07 per cent.

Benzaldehyde-benzylmercaptan, $C_6H_5 \cdot CH(S \cdot CH_2 \cdot C_6H_5)_2$, m. p. 61° . Many specimens of this compound, prepared in different ways to be described later, as well as by the direct condensation of benzyl mercaptan and benzaldehyde, have never given the melting point, 64° , stated by Fromm and Junius (*Ber.*, 1895, 28, 1111). The compound is partly hydrolysed by hydrochloric acid, yielding thereby benzaldehyde and benzyl mercaptan.

Benzyl disulphoxide, $(C_6H_5 \cdot CH_2)_2O_2S_2$, m. p. 109° . Analyses:—VII and IX from samples prepared in acetic acid solution; VIII, in alcoholic solution:

VII. 0.1626 gave 0.3612 CO_2 and 0.0732 H_2O . C = 60.57; H = 5.00.

VIII. 0.1101 „ 0.2431 CO_2 „ 0.0499 H_2O . C = 60.21; H = 5.04.

XI. 0.1307 „ 0.2210 $BaSO_4$. S = 23.20.

$C_{14}H_{14}O_2S_2$ requires C = 60.44; H = 5.04; S = 23.03 per cent.

Since these analyses were made, this compound has been described

by Fromm and Palma (*Ber.*, 1906, **39**, 3308), and more recently by Hinsberg (*Ber.*, 1908, **41**, 2836) and others, and their description agrees with my own observations.

3. *The Quantitative Results.*—The complete quantitative data will now be given. In all cases, except when otherwise stated, the reaction was carried out at the ordinary temperature, and the stream of hydrogen chloride was regulated so that no considerable heating took place.

Reaction between Benzyl Sulphoxide and Hydrochloric Acid.
Experimental Results.

Solvent.	Sulphoxide taken (grams).	Crude solid pro- ducts (grams).	Pure products (grams).						
			Ph·CHO.	Ph·CH ₂ Cl.	Ph·CH ₂ ·SH.	(CH ₂ Ph) ₂ S ₂ .	(CH ₂ Ph) ₂ S.	(CH ₂ Ph) ₂ O ₂ S ₂ .	CHPh(S·CH ₂ Ph) ₂ .
Alcohol (85 per cent.)..	20	12·1	0·4	7·1	—	2·70	2·90	5·50	—
Acetic acid (75 per cent.)	40	14·6	0·25	11·2	—	3·56	2·16	7·62	—
Glacial acetic acid	50	27·4	6·9	16·7	—	18·70	0·60	2·70	—
Glacial acetic acid + acetic anhydride	20	11·1	3·9	5·0	trace	8·75	0·10	—	1·09
No solvent	20	11·73	3·05	6·2	—	6·72	1·73	2·27	—
Water (hot)	15	10·0	3·1	1·5	trace	3·60	2·75	0·90	—
Ether (wet)	20	12·7	3·7	3·6	trace	6·27	3·86	1·32	—
Ether (dry)	20	12·6	5·7	2·0	trace	7·31	4·18	—	—
Chloroform (cold)	25	15·8	6·9	1·8	—	8·95	5·95	0·08	—
Chloroform (hot).....	20	12·7	5·8	1·2	—	6·65	5·57	—	—
Benzene	25	15·0	5·9	1·2	—	7·50	5·60	—	—
Carbon tetrachloride (hot)	25	16·0	7·3	0·3	0·3	6·35	4·75	—	0·55

In expressing these results in percentage values, the error due to unavoidable loss in the fractionation of the solid products is minimised by distributing this loss in proportion to the weights of the pure solid compounds obtained. For example, in the reaction in dry ethereal solution the solid product weighed 12·6 grams, and this on fractionation yielded 7·31 grams of benzyl disulphide and 4·18 grams of benzyl sulphide; the loss is thus 1·11 grams, and this amount, distributed proportionally to the weights of pure disulphide and sulphide obtained, raises the weights of these to 8·02 and 4·58 grams respectively.

The percentage yields in the various reactions, calculated from the above data and corrected for loss on fractionation of the solid products as just described, are given in the next table. In the last column are grouped together benzaldehyde-benzylmercaptal, benzyl

mercaptan, and the equivalent in benzaldehyde of these two, since the amounts given of the three compounds are all furnished in one reaction.

*Reaction between Benzyl Sulphoxide and Hydrochloric Acid.
Percentage Yields of Organic Products.*

Solvent.	Ph·CHO.	Ph·CH ₂ Cl.	(CH ₂ Ph) ₂ S ₂ .	(CH ₂ Ph) ₂ S.	(CH ₂ Ph) ₂ S ₂ O ₂ .	CH ₂ Ph·SH, Ph·CHO, and CHPh(S·CH ₂ Ph) ₂ .
Dilute alcohol.....	2·04	36·23	14·80	16·32	30·62	—
Dilute acetic acid	0·96	43·00	14·93	9·09	32·32	—
Glacial acetic acid	13·50	32·80	45·70	1·50	6·50	—
Glacial acetic acid + acetic anhydride.....	17·55	25·00	48·85	0·55	—	8·05
No solvent	14·54	29·56	35·05	9·02	11·83	—
Water (hot)	21·22	10·28	33·95	26·05	8·50	—
Ether (wet)	18·50	18·00	34·75	21·40	7·35	—
Ether (dry)	28·08	9·85	39·50	22·57	—	—
Chloroform (cold)	28·16	7·35	38·52	25·60	0·37	—
Chloroform (hot).....	29·44	6·09	35·07	29·40	—	—
Benzene	26·70	5·40	38·90	29·00	—	—
Carbon tetrachloride (hot)	29·92	1·25	36·48	27·28	—	5·07

4. *Explanation of the Reaction: the Hypothesis of Tautomerism.*—On the basis of the ordinarily-accepted constitutional formula for benzyl sulphoxide, namely, CH₂Ph·SO·CH₂Ph, it is not difficult to understand the formation of many of the products derived from it by reaction with hydrochloric acid. The benzyl sulphide, for example, may be regarded as a simple reduction product of the sulphoxide, and the chlorine set free in this operation could produce the disulphide and disulphoxide* by withdrawing the benzyl radicle from the sulphide or a further quantity of the sulphoxide. It is much less easy to understand the formation of benzaldehyde and benzyl mercaptan (and their condensation product, benzaldehyde-benzylmercaptan), the first of which is produced very readily in the reaction under all conditions. To account for the benzaldehyde it would be necessary to assume, first, the disruption of the sulphoxide molecule and then the combination of sulphoxidic oxygen with carbon, and

* The experiments of Fromm and Palma (*Ber.*, 1906, **39**, 3308) and Hinsberg (*Ber.*, 1908, **41**, 2836), who have lately attacked the problem of the constitution of the disulphoxides, are by no means convincing, although, on the whole, they probably favour the constitution accepted in this paper, namely,

the explanation of the formation of the mercaptan would involve the assumption of, perhaps, even less probable molecular changes.

If we assume, however, that benzyl sulphoxide may exist in the form of hydroxybenzyl sulphide, $\text{OH}\cdot\text{CHPh}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, then much of the difficulty vanishes, for a compound of this constitution might be expected to yield quite readily both benzaldehyde and benzyl mercaptan; at any rate, the formation of these two compounds from a substance of such constitution would impose no strain on the imagination. In addition, the simultaneous formation of benzaldehyde, benzyl disulphide, and benzyl sulphide would be easily accounted for.

There are thus at least two possible constitutional formulæ for benzyl sulphoxide, each of which has certain merits, in that it gives the best account of some of the products of its reaction with hydrochloric acid. Now a glance at the table of results (p. 353) reveals the fact that in seven reactions, compounds are simultaneously produced, the ready explanation of which requires the co-existence of both forms of the sulphoxide. One is thus led to the view that the sulphoxide in solution, under certain conditions, may exist in two forms, in one of which the oxygen is united with sulphur, and in the other with carbon. Further development of the subject indicates that these forms are mutually convertible, and a solution of the compound under certain conditions may be regarded as containing the dynamic isomerides in equilibrium, thus:

These forms may be called, by analogy, the ketonic and the enolic. The factors on which the equilibrium depends and the mechanism of conversion will be considered later.

On the assumption of the existence of these tautomeric forms, it is now possible to develop a series of equations expressing the reactions between one or other forms, or mixtures of both, and hydrochloric acid, which give a complete and easy account of the products formed and are verifiable by the quantitative data.

The Equations of Reaction.

- A. $4\text{CH}_2\text{Ph}\cdot\text{SO}\cdot\text{CH}_2\text{Ph} + 4\text{HCl} =$
 $\text{CH}_2\text{Ph}\cdot\text{SO}\cdot\text{SO}\cdot\text{CH}_2\text{Ph} + 4\text{CH}_2\text{PhCl} + \text{CH}_2\text{Ph}\cdot\text{S}_2\cdot\text{CH}_2\text{Ph} + 2\text{H}_2\text{O}.$
- B. $3\text{CH}_2\text{Ph}\cdot\text{SO}\cdot\text{CH}_2\text{Ph} + 2\text{HCl} =$
 $\text{CH}_2\text{Ph}\cdot\text{SO}\cdot\text{SO}\cdot\text{CH}_2\text{Ph} + 2\text{CH}_2\text{PhCl} + \text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\text{Ph} + \text{H}_2\text{O}.$
- C. $\text{CH}_2\text{Ph}\cdot\text{SO}\cdot\text{CH}_2\text{Ph} + \text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CHPh}\cdot\text{OH} + 2\text{HCl} =$
 $\text{CH}_2\text{Ph}\cdot\text{S}_2\cdot\text{CH}_2\text{Ph} + \text{CH}_2\text{PhCl} + \text{Ph}\cdot\text{CHO} + \text{H}_2\text{O} + \text{HCl}.$
- D. $2\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CHPh}\cdot\text{OH} + \text{CH}_2\text{Ph}\cdot\text{SO}\cdot\text{CH}_2\text{Ph} + 2\text{HCl} =$
 $\text{CH}_2\text{Ph}\cdot\text{S}_2\cdot\text{CH}_2\text{Ph} + 2\text{Ph}\cdot\text{CHO} + \text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\text{Ph} + \text{H}_2\text{O} + 2\text{HCl}.$
- E. $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CHPh}\cdot\text{OH} + \text{HCl} = \text{Ph}\cdot\text{CHO} + \text{CH}_2\text{Ph}\cdot\text{SH} + \text{HCl}.$

It will be noticed in these equations that the essential reaction is the reduction of the sulphoxide by hydrochloric acid, the chlorine made available for reaction by this process being employed either in oxidation of the group $\text{CHPh}\cdot\text{OH}$ to benzaldehyde, or in combining with the benzyl radicle to form benzyl chloride. In equations *D* and *E* the hydrochloric acid is completely regenerated, so that these reactions may take place without its direct intervention (its function being that of a condensing agent). In fact, equation *D* may be regarded as expressing a kind of condensation reaction between the enolic and ketonic forms of the sulphoxide, thus:

and *E*, as virtually a reaction of simple decomposition induced by the instability of the enolic form:

The latter view finds support in the reactions (to be described later) which the sulphoxide undergoes with sulphuric acid and with dehydrating agents.

It may be mentioned here that other equations have not been suggested by a careful study of the question, and that, although reaction always takes place according to more than one equation, the amount of sulphoxide decomposed according to any single equation may reach from 60 to 90 per cent. by selection of suitable conditions, and the decomposition of the enolic form into aldehyde and mercaptan by dehydrating agents is probably quantitative.

The only certain secondary reaction which takes place is that between the products from reaction *E*, which condense to form benzaldehyde-benzylmercaptan:

The chlorine set free by the oxidation of the hydrochloric acid by the sulphoxide might be thought to enter into other reactions than the two described above, and, on first consideration, might be held responsible for the tautomeric change by substitution in the sulphide, as illustrated in the following equations:

The net result of these reactions is the simple conversion of the ketonic form of the sulphoxide into the enolic. Such a process, whilst not affecting the question of the derivation of the equations, is possible, although its assumption is by no means necessary, as it will be shown later that a practically quantitative conversion of ketonic

into enolic form can be brought about by acetic anhydride, in which case there is no chance of reduction of the sulphoxide, little or no opportunity for substitution, and no water present.

The only other likely reaction for the chlorine to enter into is with benzyl mercaptan, which it might oxidise to benzyl disulphide. This reaction would take place in the following stages :

Adding these equations, together, we get :

and this is identical with equation *D*, so that any such reaction of the chlorine may be neglected.

The quantitative data may now be used for testing the hypothesis of tautomerism which has been brought forward, and which finds its expression in the five equations of reaction. The reaction in each solvent takes place in accordance with more than one equation ; there are thus several "constituent reactions" (as they may be called) which make up the complete reaction, each of which is represented by one of the equations of reaction. Some compounds are only formed in one of the constituent reactions, so that the extent to which this has proceeded is determinable ; if the complete reaction embraces another constituent reaction, the extent to which this has taken place is found by difference.

An example may be quoted to make the method of procedure clear. In dry ethereal solution the products of reaction and the percentage quantities of these are :

Benzaldehyde	28·08
Benzyl chloride	9·85
„ disulphide	39·50
„ sulphide	22·57
	100·00

No disulphoxide or mercaptan (or benzaldehyde-benzylmercaptan) is formed, so that reactions *A*, *B*, and *E* are ruled out. The benzyl chloride can only come from *C*, the sulphide only from *D*, and the other products from *C* and *D*. The percentage amounts of organic products from these two reactions are :

	<i>C</i> .	<i>D</i> .
Benzaldehyde	22·2	31·5
Benzyl chloride	26·4	—
„ disulphide	51·4	36·6
„ sulphide	—	31·9

To furnish 9·85 grams of benzyl chloride, 37·3 grams of organic products would have to be generated in reaction *C*, and the remaining

62.7 grams must thus have been produced in reaction *D*. The products would then be:

	From 37.3 grams decomposed in reaction <i>C</i> .	From 62.7 grams decomposed in reaction <i>D</i> .	Sum (calculated).	Found.
Benzaldehyde	8.28	19.75	28.03	28.08
Benzyl chloride	9.85	—	9.85	9.85
„ disulphide ...	19.18	22.95	42.13	39.50
„ sulphide	—	20.00	20.00	22.57
			100.01	100.00

and the total amount of products calculated in this way agrees satisfactorily with the experimental data.

To ascertain what amounts of benzyl sulphoxide have reacted to yield these quantities of the various products, it must be remembered that in reaction *C*, 100 grams of sulphoxide generate 104 grams of organic products, and in reaction *D*, the same amount of sulphoxide yields 97.4 grams of organic products. Consequently, 37.3 grams of products in reaction *C* arise from 35.9 grams of sulphoxide, and 62.7 grams of products in *D* from 64.4 grams of sulphoxide. Thus it follows that in the reaction between hydrochloric acid and benzyl sulphoxide in ethereal solution, 35.8 per cent. of the sulphoxide is decomposed according to equation *C*, and 64.2 per cent. according to equation *D*.

The following table gives the comparison of the experimental results with the calculations made in the manner just described. The substantial agreement of all the quantities calculated with those actually determined may be held to verify the equations, and consequently to justify the hypothesis on which they are founded.

Comparison of Experimental with Calculated Results.

		Percentage amount of organic products generated in each reaction.					
Solvent.	Percentage amount of sulphoxide decomposed in each reaction.	Ph·CHO.	CH ₂ PhCl.	(CH ₂ Ph) ₂ S ₂ .	(CH ₂ Ph) ₂ S.	(CH ₂ Ph) ₂ S ₂ O ₂ .	CHPh(S·CH ₂ Ph) ₂ , CH ₂ Ph·SH, and Ph·CHO.
Dilute ethyl alcohol.	29.1 <i>A</i>	—	14.73	7.14	—	8.07	—
	60.5 <i>B</i>	—	20.35	—	17.22	22.44	—
	10.4 <i>C</i>	2.22	2.64	5.14	—	—	—
Calculated ...	2.22	37.72	12.28	17.22	30.51	—	—
Found	2.04	36.23	14.80	16.32	30.61	—	—

Comparison of Experimental with Calculated Results (continued).

Solvent.	Percentage amount of sulphoxide decomposed in each reaction.	Percentage amount of organic products generated in each reaction.					
		Ph·CHO.	CH ₂ PhCl.	(CH ₂ Ph) ₂ S ₂ .	(CH ₂ Ph) ₂ S.	(CH ₂ Ph) ₂ S ₂ O ₂ .	CHPh(S·CH ₂ Ph) ₂ , CH ₂ Ph·SH, and Ph·CHO.
Dilute acetic acid.	63·0 <i>A</i>	—	31·40	15·30	—	17·30	—
	32·4 <i>B</i>	—	10·80	—	9·10	11·90	—
	4·6 <i>C</i>	0·95	1·14	2·21	—	—	—
	Calculated ...	0·95	43·34	17·51	9·10	29·20	—
	Found	0·96	43·00	14·93	9·09	32·02	—
Glacial acetic acid.	33·4 <i>A</i>	—	17·20	8·36	—	9·44	—
	4·9 <i>B</i>	—	1·69	—	1·43	1·89	—
	61·7 <i>C</i>	13·32	15·84	30·84	—	—	—
	Calculated ...	13·32	34·73	39·20	1·43	11·33	—
	Found	13·50	32·80	45·70	1·50	6·50	—
Glacial acetic acid + acetic anhydride.	89·8 <i>C</i>	20·01	23·78	46·31	—	—	—
	1·6 <i>D</i>	0·47	—	0·55	0·48	—	—
	8·6 <i>E</i>	—	—	—	—	—	8·10
	Calculated ...	20·48	23·78	46·86	0·48	—	8·10
	Found	17·55	25·00	48·85	0·55	—	8·05
No solvent.	31·2 <i>B</i>	—	10·85	—	9·18	11·96	—
	68·8 <i>C</i>	15·10	17·95	34·96	—	—	—
	Calculated ...	15·10	28·80	34·96	9·18	11·96	—
	Found	14·54	29·56	35·05	9·08	11·80	—
Water (hot)	21·4 <i>B</i>	—	7·79	—	6·60	8·60	—
	9·6 <i>C</i>	2·22	2·64	5·14	—	—	—
	69·0 <i>D</i>	21·11	—	24·52	21·37	—	—
	Calculated ...	23·33	10·43	29·66	27·97	8·60	—
	Found	21·22	10·28	33·95	26·05	8·50	—
Ether (moist).	18·9 <i>B</i>	—	6·78	—	5·74	7·48	—
	39·2 <i>C</i>	8·88	10·56	20·56	—	—	—
	41·9 <i>D</i>	12·60	—	14·64	12·76	—	—
	Calculated ...	21·48	17·34	35·20	18·50	7·48	—
	Found	18·50	18·00	34·75	21·40	7·35	—
Ether (dry).	35·8 <i>C</i>	8·28	9·85	19·18	—	—	—
	64·2 <i>D</i>	17·95	—	22·95	20·00	—	—
	Calculated ...	28·03	9·85	42·13	20·00	—	—
	Found	28·08	9·85	39·50	22·57	—	—
Chloroform (cold).	0·9 <i>B</i>	—	0·34	—	0·29	0·37	—
	25·3 <i>C</i>	5·88	6·99	13·62	—	—	—
	73·8 <i>D</i>	22·84	—	26·53	23·13	—	—
	Calculated ...	28·72	7·33	40·15	23·42	0·37	—
	Found	28·16	7·35	38·52	25·60	0·37	—

Comparison of Experimental with Calculated Results (continued).

Solvent.	Percentage amount of sulphoxide decomposed in each reaction.	Percentage amount of organic products generated in each reaction.					
		Ph·CHO.	CH ₃ PhCl.	(CH ₃ Ph) ₂ S ₂ .	(CH ₂ Ph) ₂ S.	(CH ₂ Ph) ₂ S ₂ O ₂ .	CHPh(S·CH ₂ Ph) ₂ , CH ₂ Ph·SH, and Ph·CHO.
Chloroform (hot).	14·2 <i>C</i>	3·33	3·96	7·71	—	—	—
	85·8 <i>D</i>	26·77	—	31·11	27·11	—	—
	Calculated ...	30·10	3·96	38·82	27·11	—	—
	Found	29·44	6·09	35·07	29·40	—	—
Benzene.	19·0 <i>C</i>	4·44	5·28	10·25	—	—	—
	81·0 <i>D</i>	25·20	—	29·28	25·52	—	—
	Calculated ...	29·64	5·28	39·56	25·52	—	—
	Found	26·70	5·40	38·90	29·00	—	—
Carbon tetra- chloride (hot).	9·4 <i>C</i>	2·22	2·64	5·14	—	—	—
	85·7 <i>D</i>	26·77	—	31·11	27·11	—	—
	4·9 <i>E</i>	—	—	—	—	—	5·00
	Calculated ...	28·99	2·64	36·25	27·11	—	5·00
	Found	29·92	1·25	36·48	27·28	—	5·07

A simple calculation from these results enables us now to accomplish a three-fold object; firstly, to attain a complete knowledge of the reaction in each solvent by determining the relative numbers of ketonic and enolic molecules which take part in each constituent reaction; secondly, to ascertain the composition at equilibrium under the particular conditions specified in each reaction; and thirdly, to bring the results into the form best suited for discussion. The method of calculation may be made clear by an example: In the five equations of reaction it will be observed that the ratio of the number of ketonic to enolic molecules is different in each case. Thus in *A* and *B* only ketonic molecules come into reaction, and in *E* only enolic molecules. The ratio of ketonic to enolic molecules in *C* is 1:1, and in *D* 1:2. Now, in the case of the reaction in moist ether, 19 per cent. roughly of the sulphoxide is transformed according to equation *B*, 39 per cent. according to equation *C*, and 42 per cent. according to equation *D*. Of 100 molecules of sulphoxide, 19 taking part in reaction *B* have thus been ketonic molecules, 19·5 each of ketonic and enolic molecules have taken part in reaction *C*, and $\frac{1}{3}$ of 42 (= 14) ketonic and $\frac{2}{3}$ of 42 (= 28) enolic molecules have reacted according to equation *D*. Tabulating these results we have:

	<i>B.</i>	<i>C.</i>	<i>D.</i>	Sum.
Percentage number of molecules of sulphoxide reacting according to equations <i>B</i> , <i>C</i> , and <i>D</i> ..	19	39	42	100
Number of ketonic molecules entering into each constituent reaction	19	19·5	14	52·5 ketonic
Number of enolic molecules entering into each constituent reaction	—	19·5	28	47·5 enolic

The percentage composition at equilibrium under the conditions obtaining in this experiment has thus been :

or, since, as will be shown later, the equilibrium has changed somewhat during the course of the reaction, these figures will represent the mean composition of the solution during the reaction.

Similar calculations for all the quantitative reactions are given in the following table :

Solvent.		Percentage number of sulphoxide molecules entering into each constituent reaction.					Sum = (percentage composition at equilibrium).
		<i>A.</i>	<i>B.</i>	<i>C.</i>	<i>D.</i>	<i>E.</i>	
Dilute acetic acid.	Total	63.0	32.4	4.6	—	—	
	Keto.	63.0	32.4	2.3	—	—	97.7 keto.
	Enol.	—	—	2.3	—	—	2.3 enol.
Dilute ethyl alcohol.	Total	29.1	60.5	10.4	—	—	
	Keto.	29.1	60.5	5.2	—	—	94.8 keto.
	Enol.	—	—	5.2	—	—	5.2 enol.
Glacial acetic acid.	Total	33.4	4.9	61.7	—	—	
	Keto.	33.4	4.9	30.8	—	—	69.1 keto.
	Enol.	—	—	30.9	—	—	30.9 enol.
No solvent.	Total	—	31.2	68.8	—	—	
	Keto.	—	31.2	34.4	—	—	65.6 keto.
	Enol.	—	—	34.4	—	—	34.4 enol.
Ether (moist).....	Total	—	18.9	39.2	41.9	—	
	Keto.	—	18.9	19.6	13.9	—	52.4 keto.
	Enol.	—	—	19.6	28.0	—	47.6 enol.
Water (hot)	Total	—	21.4	9.6	69.0	—	
	Keto.	—	21.4	4.8	23.0	—	49.2 keto.
	Enol.	—	—	4.8	46.0	—	50.8 enol.
Glacial acetic acid + acetic anhydride..	Total	—	—	89.8	1.6	8.6	
	Keto.	—	—	44.9	0.5	—	45.4 keto.
	Enol.	—	—	44.9	1.1	8.6	54.6 enol.
Ether (dry).....	Total	—	—	35.8	64.2	—	
	Keto.	—	—	17.9	21.4	—	39.3 keto.
	Enol.	—	—	17.9	42.8	—	60.7 enol.
Chloroform (cold) ...	Total	—	0.9	25.3	73.8	—	
	Keto.	—	0.9	12.6	24.6	—	38.1 keto.
	Enol.	—	—	12.7	49.2	—	67.9 enol.
Benzene	Total	—	—	19.0	81.0	—	
	Keto.	—	—	9.5	27.0	—	36.5 keto.
	Enol.	—	—	9.5	54.0	—	63.5 enol.
Chloroform (hot) ...	Total	—	—	14.2	85.8	—	
	Keto.	—	—	7.1	28.6	—	35.7 keto.
	Enol.	—	—	7.1	57.2	—	64.3 enol.
Carbon tetrachloride (hot)	Total	—	—	9.4	85.7	4.9	
	Keto.	—	—	4.7	28.6	—	33.3 keto.
	Enol.	—	—	4.7	57.1	4.9	66.7 enol.

Discussion of Results.

The expression of the quantitative results in the manner adopted in the above table brings out clearly some interesting facts connected with the reaction between hydrochloric acid and benzyl sulphoxide. It may be noted in the first place that, notwithstanding great diversities in experimental conditions, some sulphoxide has always been decomposed according to reaction *C*, into which a molecule each of the ketonic and enolic forms enters. Secondly, reaction *D* is favoured by the anhydrous solvents and by a high temperature. This may possibly be conditioned by the instability of the enolic form, the two forms reacting with each other, preferably to hydrochloric acid.

The solvents are clearly marked off into two classes, the aqueous and the anhydrous. In the former, the oxygen of the sulphoxide passes over chiefly to the disulphoxide, and in the latter, to benzaldehyde; or, looked at from another point of view, the aqueous solvents are characterised by containing a relatively high percentage of ketonic molecules at equilibrium, and the anhydrous solvents by a correspondingly large amount of enolic molecules. That the equilibrium between the two forms is brought about by a catalytic agent is a priori likely, and the facts seem to warrant the conclusion that water is the catalyst, and that the composition at equilibrium is a function of the concentration of water in the solvent.

Unfortunately, the available data concerning the solubility of water in organic liquids are of little use in this case for determining its influence exactly, because of the variation in solubility induced by the presence of hydrochloric acid and the products of its action on the sulphoxide. The general influence, however, is indisputable, and has been the subject of special study.

That the concentration of water is very low in the case of chloroform, benzene, and carbon tetrachloride, in which the percentage of enolic molecules is highest, is proved by its separating out in drops from the originally clear solution after the reaction is over. In the case of carbon tetrachloride, 150 c.c. of the dry solvent were used; the amount of water formed in the reaction from 25 grams of sulphoxide was about 0.6 gram, and judging from the appearance of the solvent after reaction, most of this water must have separated, so that its concentration would be very slight and speedily established. In dilute acetic acid and dilute alcohol, the quantity of water present from the beginning was so great that it is unlikely that the further amount formed in the reaction could have any effect on the equilibrium.

The three reactions in acetic acid show the influence of water-

concentration on equilibrium very clearly. The glacial acid used had been purified by frequent liquations from the partly frozen acid, and the relative quantities of the materials brought together were :

	Sulphoxide.	Glacial acid.	Water.	Acetic anhydride.
Dilute acetic acid	1	2.5	1	—
Glacial acetic acid	1	4.0	—	—
Glacial acetic acid + acetic anhydride	1	2.5	—	1

By reference to the figures showing the composition at equilibrium, it will be seen that the mixture of glacial acetic acid and acetic anhydride approximates in behaviour to the anhydrous solvents, which is unquestionably due to the removal of the water formed during reaction by the acetic anhydride, so that the water-concentration is kept low during the whole of the reaction. The glacial acetic acid partakes of the characters of both classes of solvents, from which it is evident that at first it acted as an anhydrous solvent, but with the progress of reaction it gradually changed its character by dissolving the water formed in the process, so that eventually it behaved more like an aqueous solvent. One may thus picture the equilibrium between the ketonic and enolic forms of the sulphoxide in glacial acetic acid as constantly changing during the reaction with hydrochloric acid, owing to the progressive conversion of enolic into ketonic molecules by the water produced in the reaction. The composition at equilibrium deduced from the data of reaction is thus a mean value.

The experiments in dry and moist ether are of particular interest in so far as they enable us to arrive at a rough quantitative estimate of the influence of water-concentration on equilibrium. In each case 20 grams of sulphoxide and 70 c.c. of ether were employed, and the reaction was carried out under similar conditions of temperature and velocity. The same sample of ether (free from alcohol) was used, the only difference being that in one experiment it was saturated with water, and in the other dried with calcium chloride and kept dry during the operation by being mixed with 4 grams of ground calcium chloride.

It is unlikely that calcium chloride, when in competition with dry hydrogen chloride for water, is so powerful a drying agent as under ordinary conditions, but it is safe to assume that the concentration of water in the "dry" ether was fairly small. The concentration in the moist ether can be calculated, knowing the solubility of water in ether and the amount of water formed in the reaction; these two quantities in the present case are 1.4 grams and 0.6 gram respectively, giving a mean value for the whole reaction of 1.7 grams or 2.4 per cent.

The ratio of the number of ketonic to enolic molecules at equilibrium in the two cases is $52.4:47.6=1:0.91$ for the moist reaction, and $39.6:60.5=1:1.55$ for the dry reaction. Thus, it follows that by diminishing the concentration of water in ether from 2.4 per cent. to a very low figure, the ratio of the number of enolic to ketonic molecules of the sulphoxide is increased in the ratio of 1:1.7.

The influence of temperature on the equilibrium of the two forms of benzyl sulphoxide, although not so closely studied as that of water-concentration, is yet clearly shown from the comparative experiments in hot and cold chloroform. From these it is obvious that increase in temperature brings about the conversion of some ketonic into enolic molecules; although having regard to the low boiling point of chloroform (61° for the pure compound; a little higher in the experiment owing to the presence of soluble substances), the effect is naturally small. It seems likely that the position of carbon tetrachloride in the list of solvents is partly due to the fact that the reaction in it was carried out at the boiling point (the sulphoxide is scarcely soluble in the solvent at the ordinary temperature). The reactions between hydrochloric acid and benzyl sulphoxide in the absence of solvent and in presence of water (that is, concentrated aqueous acid) are difficult to interpret, owing to the sulphoxide being largely attacked in each case when in the solid condition; but it seems probable that the increase of enolic molecules in the latter reaction is ascribable to the higher temperature, lessened perhaps to some extent by the influence of water on the small amount of sulphoxide dissolved.

On the question of the specific action of solvents on the equilibrium, little can be said, although there are not wanting indications that such action exists. The expectation that the mixture of acetic acid and its anhydride would have a more powerful enolising effect than the anhydrous solvents was not fulfilled, and the cause for that would appear to be inherent in the solvent. The close correspondence between enolising power and the electrolytic dissociating power of the solvents, as measured by their specific inductive capacities, points to a possible connexion between the two, and suggests that the slight apparent enolisation of the sulphoxide in the dissociating liquids may be due to the immunity from attack by hydrochloric acid conferred on the enolic form by its electrolytic dissociation. In the present state of our knowledge of the subject, however, it would perhaps be inadvisable to pursue this hypothesis further. The influence of dilution on equilibrium, which would probably throw some light on this subject, has not been studied.

The study of the reaction between hydrochloric acid and benzyl sulphoxide has thus led to the conclusion that the sulphoxide exists

in two tautomeric forms, the ketonic and the enolic, and that the equilibrium between these is dependent chiefly on the concentration of water in the solution of the compound, also on the temperature, and possibly too on the nature of the solvent. The justification of this hypothesis rests chiefly on the quantitative data, although other facts, to be detailed shortly, confirm the general view adopted. Before passing on to these, however, it may be well to mention that this case of tautomerism is peculiar, in that it involves the transference of oxygen in the molecule, and, so far as I am aware, no such case has yet been described. Considering, however, the important part which water exerts on the equilibrium of the tautomerides, this fact presents no insuperable difficulty, for the conversion of one form into the other can be conceived as the result of a succession of intermolecular reactions involving the addition and loss of water, each corresponding stage differing from its predecessor only in the mode of union or elimination of the constituents of the water. The mechanism of tautomeric change can thus be represented by a series of more or less probable reversible reactions, somewhat as follows :

There remains now only the description of some experiments performed with benzyl sulphoxide, some of which were suggested by its behaviour with hydrochloric acid, and some carried out with the view of obtaining additional evidence of its two-fold constitution.

Other Reactions of Benzyl Sulphoxide which throw Light on its Constitution.

Action of Sulphuric Acid on the Sulphoxide.—Concentrated sulphuric acid seems to have little or no action on the sulphoxide. On warming gently, the sulphoxide dissolves, and it can be recovered unaltered by pouring the solution into water. When heated at a high temperature with dilute (3 per cent.) acid, however, decomposition sets in. In a sealed tube at 170° the reaction is very slight, although the odour of mercaptan and benzaldehyde is distinct on opening the tube. At 200°, however, reaction is complete after eight hours' heating. There is no pressure on opening, which is an indication that destructive decomposition has not taken place, and the contents of the tube on steam-distillation yield a distillate composed chiefly of benzaldehyde, with a little mercaptan, and a non-volatile residue which can be resolved into benzyl disulphide and benzyl sulphide. From the original sulphoxide about one-third of the weight each of aldehyde and disulphide, and a little less than a third of sulphide, were obtained.

A small, but distinct, amount of hydrogen sulphide is also formed in this reaction. From these results it is clear that the sulphoxide has reacted with water just as it does with hydrochloric acid in equations *D* and *E*, the only two of the equations of reaction, it may be noted, in which no benzyl chloride is produced; further, to react as in these two equations, the sulphoxide must have been present both in the enolic and ketonic forms, and as the reaction took place without the agency of hydrochloric acid, additional evidence is thus afforded for the view adopted concerning the catalytic action of water.

Destructive Distillation of Benzyl Sulphoxide.—The experiments of Fromm and Achert (*Ber.*, 1903, **36**, 534) on this subject may be quoted here, because the ready formation of benzaldehyde led these investigators to doubt the usually accepted constitution of the sulphoxide. At 210° the pure sulphoxide decomposes, yielding benzyl disulphide, toluene, benzaldehyde, and sulphur dioxide. In discussing these results, Fromm and Achert say: "The remarkable decomposition of benzyl sulphoxide at 210°, and in particular the formation of benzaldehyde, raises doubt as to whether the constitutional formula $(C_6H_5 \cdot CH_2)_2S:O$, ascribed to the sulphoxide, is the right one; if it be so, then transference of oxygen from sulphur to carbon must have taken place. Such an assumption is unnecessary if oxygen is combined with carbon in the sulphoxide in a manner expressed by the formula $C_6H_5 \cdot CH_2 \cdot S \cdot O \cdot CH_2 \cdot C_6H_5$." The reduction of the sulphoxide with zinc and hydrochloric acid yields, however, benzyl sulphide, and not a mixture of benzyl mercaptan and benzyl alcohol, as would be expected with a compound of this constitution, so that the authors say, in conclusion, "Es muss also trotz der eigenartigen Zersetzung des Benzylsulfoxyds bei 210° bei der alten Formel bleiben."

It is hardly necessary to add that the enolic formula proposed in this paper represents the sulphoxide as containing oxygen combined directly with carbon, and thus in a favourable position for the formation of benzaldehyde on disruption of the sulphoxide molecule. The easy formation of sulphur dioxide, which is quite as remarkable in its way as that of benzaldehyde, would, on the other hand, be more natural to a compound having the ordinary ketonic structure of the sulphoxide; so far, then, as reactions of destructive decomposition of compounds throw light on their constitution, the results of the dry distillation of benzyl sulphoxide may be held to confirm the hypothesis of ketonic and enolic structure which has been advanced.

Action of Acetic Anhydride on Benzyl Sulphoxide.—The study of the action of hydrochloric acid on the sulphoxide having shown that, with increasing temperature and decreasing water-concentration, more and more sulphoxide reacts in the enolic form, and as this form tends

to decomposition into benzaldehyde and benzyl mercaptan, as in equation *E*, it was thought that a complete resolution of the sulfoxide into its proximate constituents might be attainable by heating it with a dehydrating agent, especially as the condensation of these constituents under the influence of the dehydrating agent might be expected to take place and to be a factor in promoting the reaction. This influence has been justified by experiment. Fifteen grams of benzyl sulfoxide and 25 c.c. of acetic anhydride were heated in a sealed tube for five hours at 150°. There was no pressure on opening the tube. Steam distillation yielded an oil containing a trace of benzyl mercaptan, a considerable amount of benzaldehyde (which was separated with sodium hydrogen sulphite), and also of another liquid with a powerful mercaptan-like odour, which did not decolorise iodine. This liquid boils at a high temperature (about 250°) with slight decomposition, and does not solidify in a freezing mixture. Although it has not yet been obtained in a condition pure enough for analysis, hydrolytic experiments show that it is in all probability benzyl acetyl sulphide, $C_6H_5 \cdot CH_2 \cdot S \cdot CO \cdot CH_3$. The residue from the steam distillation on recrystallisation yielded pure benzaldehyde-benzylmercaptan (m. p. 61°), and was quite unmixed. The meaning of this reaction seems fairly clear. Under the combined influence of the high temperature and the dehydrating agent, the benzyl sulfoxide has become completely converted into the enolic form. It has then suffered rupture with formation of benzaldehyde and benzyl mercaptan, thus :

These products have been condensed in part to the mercaptal :

the water being absorbed as soon as formed by the acetic anhydride. Apparently, also, some mercaptan has been condensed with acetic anhydride, yielding benzyl acetyl sulphide :

and benzaldehyde has been left in excess from these two main reactions.

Action of Benzoyl Chloride on Benzyl Sulfoxide.—Additional evidence of the enolic form of the sulfoxide was sought for in the reaction with benzoyl chloride. There is no apparent reaction, however, when these compounds are brought together according to the Schotten-Baumann method, but when heated in presence of carbon tetrachloride complete decomposition of the sulfoxide is effected. Twenty-five grams of benzoyl chloride and 150 c.c. of carbon tetrachloride were heated for some hours in a reflux apparatus fitted with traps, so that any moisture present in the apparatus and materials was eliminated, and the hydrochloric acid

produced was absorbed. After cooling, 20 grams of dry sulphoxide were added to the liquid. On again heating, a steady stream of hydrogen chloride was evolved, and this continued for about twelve hours. The contents of the flask were then shaken with small quantities of sodium hydroxide solution to decompose excess of benzoyl chloride, and distilled in a current of steam. Treatment of distillate and residue in the usual way yielded relatively large amounts of benzaldehyde and benzaldehyde-benzylmercaptal, and smaller quantities of benzyl disulphide, benzyl sulphide, and benzyl mercaptan, with possibly a little benzoyl benzyl sulphide, and apparently no benzyl chloride, or, at most, a trace. The reaction, in the main, thus resembles the foregoing one. Under the combined influence of the dehydrating agent and a moderately high temperature, the benzyl sulphoxide has become largely converted into the unstable enolic modification, which has decomposed into benzaldehyde and benzyl mercaptan. These have then condensed together to form benzaldehyde-benzylmercaptal, an equivalent of aldehyde remaining uncombined. The water eliminated in this reaction has decomposed some benzoyl chloride, and part of the hydrochloric acid produced thereby has reacted with the unaltered sulphoxide according to reaction *D* (and possibly to some extent, *E*), furnishing thus the disulphide and the sulphide, and setting free an additional quantity of benzaldehyde. The supply of benzaldehyde has further been supplemented by a small amount—equivalent to the mercaptan left uncombined in the first reaction of condensation.

The reaction therefore with benzoyl chloride, although it has failed to furnish the benzoyl benzyl sulphoxide, which it might have been expected to yield with a secondary alcohol of the constitution ascribed to the enolic form of benzyl sulphoxide, has nevertheless supplied evidence in favour of this constitution, and in harmony with the results of many other reactions which have been already described.

Some Miscellaneous Reactions.—For convenience sake, some properties and reactions of benzyl sulphoxide which have been noted and studied in the course of this work, but which have thrown little light on the main problem, may be mentioned here.

In the preparation of the sulphoxide by the oxidation of the sulphide with nitric acid (sp. gr. 1.3), a considerable quantity of benzaldehyde is always produced, no matter how pure the materials may be. Having regard to the instability of the enolic form of the sulphoxide, it was thought that this benzaldehyde might arise from the decomposition of the sulphoxide, and experiment shows this to be the case. This reaction is strikingly shown by chromic acid, for on gently warming a little sulphoxide with an aqueous solution of the acid in a test-tube, the odour of benzaldehyde is almost immediately observed.

The ready oxidation of the sulfoxide to sulphone by chromic acid and potassium permanganate in acetic acid solutions may again be partly conditioned by the ketonic structure of the compound in the solutions of that acid.

The small, although distinct, solubility of benzyl sulfoxide in water (roughly estimated as 0.4 per cent.), whereby it differs from the other sulphur compounds dealt with in this paper, may possibly be connected with its enolic structure.

The sulfoxide gives no colour reactions with ferric chloride, and apparently cannot be alkylated, nor does it seem to combine with phenylcarbimide, either at the ordinary temperature or when heated with it in chloroform solution in a sealed tube at 100° for twenty hours. It is impossible, however, to appraise the value of this negative evidence as yet.

The formulation of benzyl sulfoxide as a secondary alcohol ($\text{OH}\cdot\text{CHPh}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$) has suggested its derivation by reduction of the corresponding ketone, benzoyl benzyl sulphide ($\text{COPh}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$), and many experiments have been carried out with the view of proving this relationship. The ketone, however, is extremely unstable, and is reduced with disruption of the molecule even by mild reducing agents, the first products of decomposition being apparently benzaldehyde and benzyl mercaptan. This subject is still under investigation.

Conclusions.

To sum up the chief results of this investigation, the reactions of benzyl sulfoxide are best interpreted on the assumption that its structure is two-fold, the varieties differing in the disposition of the oxygen atom in the molecule, and being convertible into one another after the manner of dynamic isomerides. On the basis of the hypothesis of tautomerism proposed, it is possible to develop a series of equations representing the action of hydrochloric acid on each form (ketonic and enolic) of the sulfoxide, and on mixtures of the two forms, which not only give a clear account of the production of the many products in this somewhat complicated reaction, but also enable the hypothesis to be tested, by comparison of the quantitative data of reaction with the results calculated from these equations. The agreement of experimental with calculated values in each of twelve reactions, carried out under different conditions, may be held to justify the hypothesis.

The quantitative data enable the equilibrium between the two forms to be determined under certain specified conditions, and the conclusion is reached that this equilibrium is dependent chiefly on the temperature and the concentration of water in the solvent. Increase of

temperature and decrease of water-concentration favour the existence of the enolic modification.

The enolic form is comparatively unstable, and, on breaking up, yields benzaldehyde and benzyl mercaptan; these products, or derivatives of them, are thus formed with ease when the sulphoxide is placed under conditions favourable to the development of the enolic modification, for example, when heated with dehydrating agents like acetic anhydride and benzoyl chloride.

Finally, this case of tautomerism is peculiar in that change from one form to another involves the transposition of the oxygen atom in the molecule.

ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE.