CXIII.—*Diethoxythioxan; a Relation between the Refractive Power and Chemical Activity of some Sulphur Compounds.*

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THE experiments described in this paper were originally undertaken with the intention of examining thiazine, the parent substance of the dibenzothiazine derivatives which have been recently studied by one of the present authors and T. P. Hilditch (Trans., 1908, **93**, 145, 1687). So far as this object is concerned, the results have not yet been successful; in fact, our progress along the lines of investigation which we originally planned has been barred by the unexpected stability of one of the intermediate products. The latter substance, which is a saturated cyclic sulphide, seemed of interest on account of the comparatively inert state of the bivalent sulphur atom contained in it, and we therefore examined more closely the chemical activity of the compound. The results of this investigation are described in the following pages, and finally we offer what appears to us to be the only rational explanation of the anomaly.

By the interaction of sodium sulphide and chloroacetal, the acetal sulphide (I) is formed in the usual manner, and it was hoped that by the action of ammonia on this, under suitable conditions, the imino-group might be introduced, forming the thiomorpholine derivative (II). Acetal sulphide, however, seems very stable towards alkaline reagents, and experiments in this direction have not led to the desired result.

On the other hand, acetal sulphide is immediately attacked by cold mineral acids, as indeed might be expected from the presence of the acetal grouping. But in these reactions the aldehyde which we hoped easily to convert to the required nitrogen derivative is not formed, the product being the cyclic compound* (IV), which no doubt is produced by elimination of water from the alcoholate (III).

(I.)

(II.)

(III.)

(IV.)

So far as we are aware, the only other derivatives of thioxan which have been met with are the so-called diethylene oxide sulphone, which Baumann and Walter (*Ber.*, 1893, **26**, 1138) obtained by the action of barium hydroxide on diethylene disulphone and the anhydride of thiodiglycollic acid (Anschütz and Biernaux, *Annalen*, 1893, **273**, 68); but these substances were not very fully investigated. The diethoxythioxan which we have obtained in the previously described manner is worth especial notice on account of its well-defined physical properties, its general stability, and the depressed reactivity of the sulphur in comparison with that of the corresponding open-chain compound. We have paid especial attention to the last-named property.

The open-chain compound, acetal sulphide, shows all the usual properties of a substance in which bivalent sulphur is united to

* Structures such as that of the monoaldehyde and others cannot be entertained, since the substance is devoid of the usual reducing properties of aldehydes and α -ketols, and does not yield a hydrazone or acyl derivatives.

saturated hydrocarbon groups; for example, it furnishes additive products with mercuric chloride and iodide, it is oxidised by hydrogen dioxide at the atmospheric temperature to a sulfoxide, and, under certain conditions, it combines readily with alkyl iodides. On the other hand, diethoxythioxan neither combines with mercuric halides nor reacts with hydrogen dioxide under the conditions chosen for comparison, and even in the presence of mercuric iodide the addition of alkyl iodide proceeds extremely slowly.

These comparative data are summarised in the following table, and, in order to show the normal character of acetal sulphide, the reactions of another sulphide of high molecular weight are inserted. Dibenzyl sulphide is chosen for this latter comparison:

Reagent.	Result with		
	Dibenzyl sulphide.	Acetal sulphide.	Diethoxythioxan.
HgCl ₂ or HgI ₂ and acetone or alcoholic solution.	Immediate formation of (CH ₂ Ph) ₂ S·HgX ₂ [(CH ₂ Ph) ₂ S·HgX ₂ (Trans., 1900, 77 , 165).	Immediate formation of (EtO) ₂ CH·CH ₂] ₂ S·HgX ₂	No reaction detected.
H ₂ O ₂ (excess) in acetone solution for three days at ordinary temperature.	Almost quantitative formation of (CH ₂ Ph) ₂ SO (Gazdar & Smiles, Trans., 1908, 93 , 1833).	Sulfoxide formed, apparently quantitative.	Almost all the original compound was isolated unaltered.
Excess of ethyl iodide and one molecular proportion of HgI ₂ at the atmospheric temperature.	Formation of (CH ₂ Ph) ₂ SEtI, HgI ₂ complete in five hours (Hilditch & Smiles, Trans., 1907, 91 , 1393).	Good yield of sulphonium salt obtained in five hours.	After eight hours, no sulphonium salt could be detected, and after 24 hours, only a small amount.

The results of the last-named reaction are the most interesting. It has been shown elsewhere (Smiles, Trans., 1900, **77**, 163; Hilditch and Smiles, Trans., 1907, **91**, 1393) that the addition of mercuric halide to a mixture of alkyl halide and sulphide enormously accelerates the formation of the sulphonium salt; in fact, it has been shown that the union of ethyl iodide and dimethyl sulphide, which in ordinary circumstances is scarcely complete in three days, may be effected in about fifteen minutes if mercuric iodide be present. At one time or another, one of the present authors has examined about fifteen of these reactions with saturated sulphides, and the thioxan derivative now described stands out as by far the most sluggish of all of them.

In attempting to find some explanation of the comparative inactivity of the sulphur in this substance, it is natural to turn first to the hypothesis of steric hindrance, since this has usually been employed to account for the depressed activity of a group.

But it is evident that the usual theories do not apply in this case, for the only substituents in the thioxan system are not adjacent to the sulphur atom. Moreover, to assume that the thioxan ring is so distorted as to prevent the addition of groups to the sulphur atom appears to us to be quite unjustifiable, although it must be admitted that little is yet known of the steric conditions of heterocyclic systems. For these reasons, we consider that steric hindrance cannot be applied to explain the anomalous behaviour of this substance. But a satisfactory explanation is furnished by considerations similar to those employed by Thiele (*Annalen*, 1899, **306**, 87; **308**, 333) in accounting for the inert state of the central carbon atoms of a conjugated system of two ethenoid linkings. It is well known that here the partial valencies or residual affinities of these carbon atoms are supposed to satisfy each other, so that additive reagents are not taken up at this point, but at the first and fourth carbon atoms of the chain.

That the bivalent sulphur in saturated hydrocarbon sulphides is endowed with residual affinity has been evident since the earliest researches on these compounds, when their additive reactions were discovered, and since the work of Collie and Tickle on dimethylpyrone (*Trans.*, 1899, **75**, 710) and of Friedel on dimethyl ether (*Bull. Soc. chim.*, 1875, [ii], **24**, 160, 241), the same has been admitted for bivalent oxygen.

Making this assumption of the unsaturated nature of the sulphur and oxygen—and it scarcely can be disputed—we advance as an explanation of the inactivity of the sulphur the hypothesis that the residual affinities of these elements partially saturate one another, and since the usual formulæ are insufficient to represent this state, we suggest that this thioxan derivative should be represented as follows (V):

If the justice of hypotheses such as that put forward by Thiele be admitted, the only objection which can be raised against the present scheme is that the elements the residual affinities of which are combined are in the 1:4-positions of a six-membered ring instead of being adjacent. But this difficulty is readily overcome when it is remembered that much evidence has already been

collected to show that unsaturated atoms in this 1 : 4-position of a six-membered ring system are peculiarly liable to influence one another, and in some cases combination by means of the usual valencies has been observed. In fact, in the light of this evidence, it appears probable that some connexion between unsaturated atoms in this position should exist. In the case of homocyclic compounds, it is sufficient to recall the researches of Collie (Trans., 1897, **71**, 1013) and of Baly, Edwards, and Stewart (Trans., 1906, **89**, 514) on the mobility of the benzene system. The latter-named investigators showed (*loc. cit.*, p. 525) that at a certain phase in the pulsation of the system the residual affinities of the 1 : 4-atoms will temporarily saturate each other, and this afforded an explanation of the previously observed tautomerism of phenol (Baly and Ewbank, Trans., 1905, **85**, 1348); also there is spectroscopic evidence to show (Stewart, *Stereochemistry*, 1907, p. 486) that the carbonyl groups in *cyclohexan-1 : 4-dione* influence each other in such a way as to cause abnormal reactivity. With regard to heterocyclic systems, it may be observed that Dewar (*Zeitsch. Chem.*, 1871, **7**, 117) and Riedel (*Ber.*, 1883, **16**, 1609) entertained the idea that the nitrogen and γ -carbon atoms of the pyridine nucleus are united; further, that the usually accepted formula for acridine shows the union between the nitrogen and *meso*-carbon atom, and that the alternative formula for pyrazine and its derivatives shows a similar union between the nitrogen atoms. Finally, it may be mentioned that the recent work of Collie on dimethylpyrone has shown that a close relation exists between the carbonyl group and the cyclic oxygen.

The thioxan derivative which we have examined is not the only bivalent sulphur compound of abnormal properties. The case of thiophen is of particular interest in the present discussion, since, like thioxan, it contains other unsaturated atoms besides sulphur. The attempts made by Victor Meyer and his pupils (*Die Thiophengruppe*, Braunschweig, 1888) to combine this substance with alkyl iodides were unsuccessful, and oxidation experiments to obtain the sulphone met with similar results. In fact, the sulphur in thiophen closely resembles in chemical character that of diethoxythioxan, and similar considerations give a satisfactory explanation of its inactivity. So far as the state of the sulphur is concerned, the thiophen molecule is well represented by some formula, such as that written above (VI), which shows the residual affinity of that element to be partly saturated by that of the adjacent carbon atoms. Other examples of compounds containing sulphur of subnormal activity are the aromatic sulphides, and these also contain unsaturated groups adjacent to the sulphur.

We have also examined the refractive power of diethoxythioxan and the other sulphur compounds previously mentioned, and the evidence thus obtained supports the conclusions made from the chemical behaviour of the substance. Brühl has concluded (*Ber.*, 1907, **40**, 878, 1153), from a general survey of the refractivities of unsaturated compounds, that the refractive power of these substances is abnormal if the unsaturated groups are adjacent, or, using the term introduced by Thiele, if these groups are conjugated. Brühl seems to have applied the term conjugated to any system of unsaturated atoms or groups the residual affinities of which exert a mutual influence; and in this sense, which we consider desirable, the application of the term is wider than that originally made by Thiele. It may be mentioned that Brühl has drawn attention (*loc. cit.*, p. 1154) to a few exceptions to his rule, nevertheless optical anomaly has been generally accepted by chemists as an excellent supplement to chemical evidence in detecting the presence of "conjugated" atomic groupings.

The relations discovered by Brühl with carbon, nitrogen, and oxygen compounds hold also with sulphur compounds in which unsaturated atoms are adjacent to this element. Indeed, Brühl has already drawn attention to the behaviour of thiophen, which shows a remarkable depression in molecular refractive power:

Thiophen.	M_α (obs.).	M_α (calc.).	Δ .
C_4H_4S	24.14	25.40	1.26

Also diphenyl sulphide, which reacts sluggishly with alkyl iodides (Schöller, *Ber.*, 1874, **7**, 1274) and mercuric halides, shows optical anomaly. The refractive index of this substance was determined by Gladstone (*Journ. Chem. Soc.*, 1870, **23**, 147):

	M_α (obs.).	M_α (calc.).	Δ .
Diphenyl sulphide, $C_6H_5 \cdot S \cdot C_6H_5 \dots$		$2 \times C_6H_5 = 51.86$	
		Less $2H = 2.20$	
		<hr/>	
		49.66	
		$S \text{ as in } Et_2S = 8.00$	
		<hr/>	
	58.97	57.66 + 1.31	

Another aromatic sulphide may be added as a further example:

	M_α (obs.).	M_α (calc.).	Δ .
Dihydroxydiphenyl sulphide, $S(C_6H_4 \cdot OH)_2$		$2 \times C_6H_4 \cdot OH = 55.50$	
		Less $2H = 2.20$	
		<hr/>	
		53.30	
		$S \text{ as in } Et_2S = 8.00$	
		<hr/>	
	65.16	61.30 + 3.86	

The refractivity of diallyl sulphide has been measured by Nasini and Scala (*Gazzetta*, 1887, **17**, 76):

	M_a (obs.).	M_a (calc.).	Δ .
Diallyl sulphide, $(C_3H_5)_2S...$	36.73	Sum of atomic * refractivities = 36.79	- 0.06

The data show this compound to be normal, and since there is no direct chemical proof whether it has the structure:

the former alternative may be adopted as conforming to the optical evidence. As bearing on this question, it may be mentioned that Eykman has deduced from refractivity data (*Chem. Weekblad*, 1906, **3**, 711) that allyl cyanide has the structure: $CH_2:CH \cdot CH_2 \cdot CN$. In correspondence with the normal refractive power of allyl sulphide, the reactivity of the sulphur is normal, for Semmler (*Annalen*, 1887, **241**, 118) has obtained a mercuric chloride additive product, and diallylsulphonium salts have been prepared (Cahours, *Zeitsch. Chem.*, 1865, 438; and Bayer and Co., 1898, D.R.-P. 97207).

Turning now to the thioxan derivative and the substances of normal reactivity with which it is compared in the table, it is found that the latter compounds are optically normal, whilst diethoxythioxan is slightly abnormal:

	M_a (obs.).	M_a (calc.).	Δ .
Dibenzyl sulphide, $(C_6H_5 \cdot CH_2)_2S$		$2 \times C_6H_4Me = 61.58$	
		Less 2H = 2.20	
		<hr/> 59.38	
		S as in $Et_2S = 8.00$	
		<hr/> 67.38	
	67.42		67.38 + 0.04

The contrast between this normal sulphide and phenyl sulphide is worth special mention. In the latter substance, the bivalent sulphur atom is directly united with the unsaturated carbon atoms of the benzene nuclei, the reactivity and refractive power are consequently abnormal; but in the normal benzyl sulphide the sulphur is isolated from each benzene nucleus by an intervening saturated group.

In calculating the refractivity of acetal sulphide, the value

* In all these calculations, the atomic refractivity of sulphur employed is that deduced from Nasini's measurement (*Ber.*, 1882, **15**, 2878) of the refractive power of diethyl sulphide. The reactivity of this substance is normal. The values quoted for dibenzyl sulphide and dihydroxydiphenyl sulphide are those observed by Nasini and are taken from his article on the subject in *Nuova Enciclopedia di Chimica*, I, 792 (1906).

found by Brühl (*Zeitsch. physikal. Chem.*, 1891, **7**, 160) for acetal has been employed.

	M_a (obs.).	M_a (calc.).	Δ .
Acetal sulphide, $C_{12}H_{26}O_4S$		$2 \times \text{acetal} = 65.76$	
		Less $2H = 2.20$	
		<hr/> 63.56	
		$S \text{ as in } Et_2S = 8.00$	
	71.61	<hr/> 71.56	+ 0.05

Here again the refractive power and chemical activity are normal.

	M_a (obs.).	M_a (calc.).	Δ .
Diethoxythioxan, $C_8H_{16}O_3S$.	In methylal, 49.94	Acetal sulphide, 71.61	
	In CCl_4 , 49.85	Less $C_4H_{10}O < 22.15$	
	In CCl_4 , 49.79		
	Average = 49.86	<hr/> 49.46	+ 0.40

In calculating the values for acetal sulphide and diethoxythioxan, we have avoided the usual method of adding together the atomic effects, since in complex substances which contain so many atoms in the molecule the slight errors involved in the atomic refractivities are multiplied many times. We have instead used the method which Eykman (*Rec. trav. chim.*, 1893, **12**, 157, 268) emphatically recommends on other grounds; thus the refractive power of a substance closely allied to the compound in question is taken as a basis and then modified in the required manner. It is also necessary to point out that in calculating the value for diethoxythioxan from that of acetal sulphide we have assumed that ring formation has no effect; this is in harmony with the assumption generally made in refractometric work, and it is further justified by the work of Brühl on epichlorohydrin (*Ber.*, 1891, **24**, 657) and paracetaldehyde (*Annalen*, 1880, **203**, 43), in which the formation of oxygen rings was shown to have no effect on refractivity. The formation of cyclic systems has been studied also by Eykman (*Ber.*, 1892, **25**, 3069) in the piperidine series, and by Willstätter (*Ber.*, 1907, **40**, 3982) and Wallach (*Annalen*, 1907, **353**, 331) in the *cycloparaffins*, and these observers agree that cyclic formation is without effect on the refractive power.

It must be admitted that with the thioxan derivative the difference between the calculated and observed values is small—about 0.4 unit—in comparison with that observed with the other sulphur compounds. But the value which we quote is the mean of three observations, each with different samples of the substance and in different solvents; moreover, the anomaly is of the same order as that observed by Brühl in pyrrole (-0.37), acrolein ($+0.34$), ethyl

crotonate (+0.44), and other carbon compounds. We therefore consider that diethoxythioxan shows a small but quite perceptible exaltation.

The general conclusions to be drawn from the refractivities of these bivalent-sulphur compounds is that a normal or abnormal state of the reactivity of the sulphur is accompanied by a corresponding state of the refractive power of the substance; but at present it is impossible to say whether any quantitative relation holds between the chemical and the physical anomaly.

Leaving the thioxan derivative for a moment out of the question, it is further evident that all the substances dealt with conform to the law laid down by Brühl, since the abnormal compounds contain the bivalent sulphur adjacent to other unsaturated atoms and the normal ones do not. Moreover, the depressed reactivity of the optically anomalous compounds may be explained by the assumption that the residual affinity of the bivalent sulphur which endows this element with additive properties is at least partly saturated by that of the adjacent unsaturated atoms.

In the light of this evidence, taken from various types of bivalent-sulphur compounds, the step to the thioxan derivative is clearly indicated. Thus it seems that the unsaturated sulphur of this compound must be "conjugated" with another unsaturated group, which, from reasons previously mentioned, is probably the cyclic oxygen in the 1:4-position with respect to the sulphur atom.

EXPERIMENTAL.

Acetal Sulphide.—An alcoholic solution containing 50 grams of chloro-acetal with about one and a-half times the calculated quantity of sodium sulphide was heated on the water-bath for twenty-four hours. The alcohol was then removed by distillation, and the residue faintly acidified with dilute sulphuric acid. The free hydrogen sulphide remaining in solution was expelled by blowing a rapid current of air through the mixture at the atmospheric temperature. Finally the oily layer, which consisted of the required sulphide and unchanged chloroacetal, was separated by repeated extraction with ether. The united extracts were dried and distilled, first on the water-bath, and finally under diminished pressure. The yield was about 30 grams of acetal sulphide, a colourless oil boiling at 147—148°/12 mm.:

0.1028 gave 0.2021 CO₂ and 0.0874 H₂O. C=53.6; H=9.44.

C₁₂H₂₆O₄S requires C=54.1; H=9.77 per cent.

The refractive index and density of a pure sample were determined:

$$d_{23.5^{\circ}} = 0.9863; \quad d_{17.5^{\circ}} = 0.9918.$$

$$n_{D(23.5^{\circ})} = 1.44734; \quad n_{a17.5^{\circ}} = 1.44659.$$

whence, according to the Lorenz-Lorentz formula, the molecular refractive power is:

$$M_D = 71.95 \quad \text{and} \quad M^a = 71.61.$$

Additive products with mercuric halides.—An aqueous-alcoholic solution of acetal sulphide, when mixed with mercuric chloride solution, at once yields a precipitate of the double salt. A sample of this substance was recrystallised from alcohol, and was thus obtained in well-defined needles, which melted at 70° :

0.1888 gave 0.1848 CO_2 and 0.0792 H_2O . $\text{C} = 26.71$; $\text{H} = 4.66$.

$\text{C}_{12}\text{H}_{26}\text{O}_4\text{S}, \text{HgCl}_2$ requires $\text{C} = 26.81$; $\text{H} = 4.84$ per cent.

Acetal sulphide mercurichloride is insoluble in water, and easily soluble in alcohol or acetone.

Mercuric iodide, when shaken with an acetone solution of acetal sulphide at the atmospheric temperature, gives a copious, crystalline precipitate of the double salt. It melts at 68° , and is sparingly soluble in ether or in cold alcohol; when set aside the substance decomposes into the constituents.

Action of Ethyl Iodide on Acetal Sulphide in Presence of Mercuric Iodide.

Equimolecular proportions of acetal sulphide and mercuric iodide were shaken at the atmospheric temperature with an excess of ethyl iodide (10 c.c. for every gram of acetal sulphide). In about half an hour the mercuric iodide had completely dissolved, indicating the commencement of formation of the sulphonium salt. After five hours had elapsed, the excess of alkyl iodide was removed by a rapid current of air, and the oily residue was set aside to crystallise. The semi-solid mass was repeatedly extracted with ether, which removed an unstable mercuric iodide double salt, and the residue of sulphur yellow leaflets, after further purification, was analysed:

0.1624 gave 0.1161 CO_2 and 0.0593 H_2O . $\text{C} = 19.48$; $\text{H} = 3.92$.

$\text{C}_{14}\text{H}_{31}\text{O}_4\text{I}_3\text{SHg}$ requires $\text{C} = 19.18$; $\text{H} = 3.54$ per cent.

Diacetaethylsulphonium mercuri-iodide melts at 43° , and is soluble in alcohol or acetone and sparingly so in ether. About one and a-half grams of purified material were obtained from one gram of acetal sulphide.

Acetal sulphide and excess of hydrogen dioxide were mixed in acetone solution, and kept for twenty-four hours. The oily product which remained after evaporating the solvent could not be purified, since it decomposed on being heated and could not be solidified. Attempts to convert it to solid derivatives with mercuric halides or by means of dry hydrogen chloride to obtain a thioxan derivative were also unsuccessful. Apparently the conversion of the acetal sulphide is almost complete, since no diethoxythioxan could be isolated by treatment with hydrochloric acid. The substance, which is almost certainly the sulphoxide, is distinguished from the acetal sulphide by much greater solubility in water.

Diethoxythioxan.

Dry hydrogen chloride was rapidly passed for a few minutes through a solution of acetal sulphide in absolute alcohol or dry ether. On evaporating the solvent as quickly as possible under diminished pressure, diethoxythioxan remained as a mass of colourless crystals. The reaction appears to be almost quantitative, since 2.46 grams of acetal sulphide gave 1.75 grams of thioxan derivative, whilst theory requires 1.77 grams.

The substance may be purified by crystallisation from alcohol or by sublimation, which frequently yields crystals more than one inch in length. In either case the product melts at 101° ; it is soluble in hot water and in most organic media:

0.1142 gave 0.2062 CO_2 and 0.0902 H_2O . $\text{C}=49.2$; $\text{H}=8.7$.

$\text{C}_8\text{H}_{16}\text{O}_3\text{S}$ requires $\text{C}=50.0$; $\text{H}=8.3$ per cent.

The molecular weight was determined by the cryoscopic method:

0.2691 in 16.48 benzene gave $\Delta t = -0.423^{\circ}$. M.W.=189.

$\text{C}_8\text{H}_{16}\text{O}_3\text{S}$ requires M.W.=192.

The refractivity of the substance in carbon tetrachloride and methylal was determined with purified samples from three different preparations:

I. In Carbon Tetrachloride.

Solvent: $d_{40} = 1.6014$; $n_D = 1.4587$; wt. = 8.5873.

Solution: $d_{40} = 1.5704$; $n_D = 1.4597$; wt. = 8.9590.

$M_D = 49.85$.

II. In Carbon Tetrachloride.

Solvent: $d_{40} = 1.6014$; $n_D = 1.45757$; wt. = 7.9754.

Solution: $d_{40} = 1.5484$; $n_D = 1.45921$; wt. = 8.5904.

$M_D = 49.79$.

III. *In Methylal.*

Solvent: $d_{18} = 0.86315$; $n_a = 1.35192$; wt. = 3.8958.

Solution: $d_{18} = 0.87439$; $n_a = 1.35792$; wt. = 4.1424.

$M_a = 49.94$.

Diethoxythiozan may be crystallised from a boiling 10 per cent. aqueous solution of sodium hydroxide; it does not reduce warm Fehling's solution, cold neutral or acid permanganate solutions, or ammoniacal silver solution. Also the substance is not attacked by concentrated alcoholic or aqueous ammonia at 150° ; it is very soluble in concentrated aqueous hydrochloric acid, being decomposed thereby, and on evaporating the solution under diminished pressure, an amorphous substance is deposited. Concentrated sulphuric acid freely dissolves the substance, giving a red solution. Additive products with mercuric chloride or iodide could not be obtained by mixing these substances with an acetone or alcoholic solution of diethoxythiozan; it may be recalled that such additive products are readily obtained from acetal sulphide under similar conditions.

Diethoxythiozan seems unattacked by hydrogen dioxide under the same conditions as those described with acetal sulphide, since almost the entire amount of the original material could be isolated after treatment.

Action of Ethyl Iodide in Presence of Mercuric Iodide.—A solution in ethyl iodide of diethoxythiozan (1 gram for every 10 c.c. of ethyl iodide) and mercuric iodide in equimolecular proportions was set aside at the atmospheric temperature. After eight hours, a portion of the mixture was examined, but no sulphonium salt could be isolated. In fifteen hours, there were signs that reaction had commenced, since a small quantity of the mercuric halide had passed into solution; but the mixture was not more closely examined until a further nine hours had elapsed. The liquid was then filtered from the undissolved mercuric iodide, and the ethyl iodide was removed from the filtrate by a rapid current of air. The yellow oil which remained was unstable, and, if allowed to remain exposed to the atmosphere, readily deposited mercuric iodide; but before profound decomposition had taken place, the mixture was repeatedly extracted with dry ether, and thus a stable and almost colourless solid was obtained in the proportion of half a gram to every gram of diethoxythiozan taken. After purification, it melted at $95\text{--}97^\circ$:

0.1028 gave 0.0562 CO_2 and 0.0230 H_2O . $\text{C} = 14.9$; $\text{H} = 2.48$.

$\text{C}_{10}\text{H}_{21}\text{O}_3\text{I}_3\text{SHg}$ requires $\text{C} = 14.96$; $\text{H} = 2.49$ per cent.

The additive compound is readily soluble in acetone, but almost insoluble in water of ether.

It may be mentioned that no signs of reaction between ethyl iodide and the thioxan derivative alone could be detected after the mixture had remained for four days at the atmospheric temperature.

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