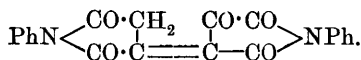


LXXIV.—*The Action of Ethyl Oxalate on Thioacetanilide and its Homologues.*

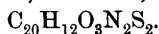
By SIEGFRIED RUHEMANN.

THE study of the behaviour of ethyl oxalate towards acetanilide and its analogues (see Ruhemann, *Trans.*, 1906, **89**, 1236, 1847) led to the knowledge of compounds the representative of which, xanthoxalanil, has the formula

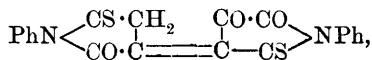


This constitution has been derived not only from the mode of formation of the substance, but also from the fact that, on hydrolysis with caustic potash, it yields dianilaconitic acid* which in turn furnishes aconitic acid on treatment with hydrochloric acid.

The results of this investigation have induced me to examine the reaction of thioacetanilide and its homologues with ethyl oxalate, and I have found that coloured compounds are formed which in composition differ from xanthoxalanil and its analogues only inasmuch as two of their oxygen atoms are replaced by sulphur. The substance which is produced from thioacetanilide, therefore, has the formula

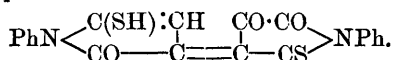


This fact leads to the conclusion that the constitution of the compound is analogous to that of xanthoxalanil, namely:

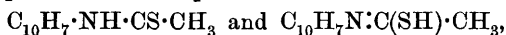


* I had pointed out before (*Trans.*, 1906, **89**, 1850) that a compound with this formula had been prepared by Michael (*Amer. Chem. J.*, 1887, **9**, 192) which, in melting point, differed by about 10° from the dianilaconitic acid obtained by me from xanthoxalanil. I have since prepared Michael's substance and find that the yield is very small, although the aqueous solution of the dianiline salt of aconitic acid had been kept for more than four weeks. A comparison of the two dianilaconitic acids has established the fact that they differ not only in their melting points, but also in their behaviour towards concentrated hydrochloric acid; this readily dissolves Michael's compound, as stated already by this chemist, whereas the other is insoluble.

and accordingly is to be called *dithioxanthoxalanil*. Similar formulæ must be assigned to the substances which are formed from the homologues of thioacetanilide. These compounds are highly coloured and sparingly soluble in most solvents. With regard to their colour I have noticed that they show similar differences from the corresponding compounds derived from acetanilide and its analogues, dithioxanthoxalanil being dark brown, whereas its homologues have a lighter shade. These thio-derivatives have no acidic properties, and in this respect resemble the other class of compounds; they differ, however, from the latter in their great stability towards alkalis. Whilst xanthoxalanil, on digestion with dilute caustic potash, is readily decomposed and yields dianilaconitic acid, dithioxanthoxalanil does not suffer a similar change under these conditions, but is transformed into its tautomeride. The fact that this substance is very soluble in dilute alkalis as well as alkali carbonates points to the formula :

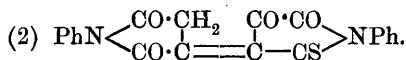
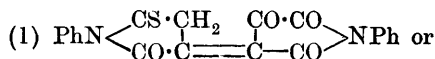


The formation of this compound is of some interest, because tautomeric forms of thioacetanilide and its homologues have not been obtained; P. Jacobson (*Ber.*, 1888, 21, 2627), indeed, stated that thioacetob-naphthalide, on rapidly cooling its alcoholic solution, crystallised in needles which changed into plates when left in the mother liquor for some time, but both kinds of crystals melted at the same temperature. This phenomenon was explained by the assumption that the different crystallographic forms corresponded to the tautomerides,



but experimental proofs in support of this view have not been brought forward.

A more profound change in dithioxanthoxalanil takes place if this compound is boiled with dilute caustic potash for several hours, when one atom of sulphur is substituted by oxygen, and a substance, *thioxanthoxalanil*, is formed which, *a priori*, may be represented either by the formula



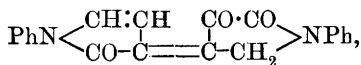
The fact, however, that this compound dissolves in sodium carbonate, whereas xanthoxalanil, which contains the group $\text{PhN} \begin{array}{c} \text{CO} \cdot \text{CH}_2 \\ \text{CO} \cdot \text{C} \end{array}$, is insoluble in this agent, points to the formula (1). Similar substances have been obtained from dithioxanthoxalo-*p*-toluidil and dithioxanthoxalo- β -naphthylamil. A complete decomposition of dithio-

xanthoxalanil is not effected until it is boiled with concentrated (60—70 per cent.) aqueous caustic potash, when aniline and oxalic acid are produced.

Of especial interest is the action of reducing agents on dithioxanthoxalanil; it has been shown previously (*loc. cit.*) that xanthoxaloxylidil, $C_{24}H_{20}O_5N_2$ (this compound had been chosen instead of xanthoxalanil on account of its solubility in glacial acetic acid), absorbs 6 atoms of hydrogen, and yields a colourless substance of the formula $C_{24}H_{26}O_5N_2$. Dithioxanthoxalanil, however, by the action of zinc dust and acetic acid, is transformed into a compound which has the composition $C_{20}H_{16}O_3N_2$, indicating that the sulphur is entirely replaced by hydrogen, and that no addition of hydrogen takes place. On the one hand, the fact that the substance is insoluble in cold alkalis or cold alkali carbonates, on the other that it is almost colourless, leads to the view that the substitution is accompanied by a change in the linking. Its formation is probably to be interpreted thus: dithioxanthoxalanil first changes into its tautomeride:

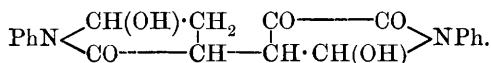


this subsequently is transformed into:



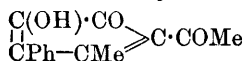
which finally is reduced to $\text{PhN} \left\langle \begin{array}{c} \text{CH}_2\text{·CH} \\ \text{CO—C} \end{array} \begin{array}{c} \text{CO—CO} \\ \text{CH·CH}_2 \end{array} \right\rangle \text{NPh}.$

Experiments are in progress with the object of verifying this constitution, and also of ascertaining whether the conclusion which may be drawn from the behaviour of dithioxanthoxalanil with regard to the structure of the reduction product of xanthoxalanil is correct. The fact that the group ·CO·CO· is not altered in the course of the reduction of the thio-compound would suggest that it is not changed in the other case, and that the compound $C_{24}H_{26}O_5N_2$ is accordingly to be represented thus:



The reduction product, $C_{20}H_{16}O_3N_2$, of dithioxanthoxalanil is characterised by its behaviour towards alkalis or alkali carbonates. Although these reagents have no effect on the compound at the ordinary temperature, yet on boiling they transform it into a blue solid. This product is the alkali derivative of a cherry-red compound which is formed on adding dilute hydrochloric acid to the blue substance. I have not yet been able to complete the study of this red compound owing to the small yield of the reduction product $C_{20}H_{16}O_3N_2$, but there seems to be no doubt that it is isomeric with

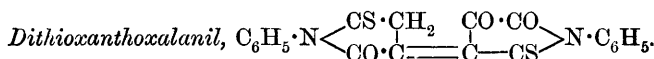
the latter substance. This reaction resembles the transformation which the yellow product of the reaction between acetylacetone and phenylpropiolyl chloride suffers under the influence of organic bases as well as sodium carbonate, and which yields the red substance



(Ruhemann and Merriman, *Trans.*, 1905, **87**, 1383). This also forms blue salts, as does Claisen and Ewan's oxalydibenzyl ketone and triethyl anhydro-oxalaconitate (*loc. cit.*).

The analogy in the behaviour of these substances points to the view that the red compound which is formed from the reduction product of dithioxanthoxalanil under the influence of alkalis possesses a similar constitution. It differs from the other compounds of this type inasmuch as it is more stable both towards alkalis and alkali carbonates.

EXPERIMENTAL.



This substance is prepared by adding ethyl oxalate (20 grams) to sodium ethoxide (9 grams) suspended in dry benzene and mixing the solution with thioacetanilide (20 grams) dissolved in benzene. After a short time a yellow solid separates which undoubtedly is the sodium derivative of thioacetanilide. This disappears in the course of several hours, and a deep red solution is formed which, on standing overnight, sets to a semi-solid mass of red crystals. These have not been examined, because they are very hygroscopic, and on attempting to collect them are transformed into a gelatinous mass. On adding water to the product of the reaction, the solid readily dissolves, yielding a red solution which is separated from the benzene layer and treated with an excess of dilute hydrochloric acid; a cloudiness is produced which after a short time coalesces into a red solid. The precipitate is washed with water, then with alcohol, and dried in the steam-oven. The original aqueous filtrate and the dark alcoholic washings deposit a further amount of the substance in the course of a few days. The compound is insoluble in alcohol, fairly soluble in hot benzene, and very sparingly so in boiling glacial acetic acid; 5 grams require more than 1 litre of the solvent to yield a deep red solution, from which, on cooling, beautiful, brown prisms separate. The yield of the recrystallised substance amounts to about 50 per cent. of the weight of thioacetanilide. Dithioxanthoxalanil has no definite melting point; it darkens above 200° and decomposes at about 235° with evolution of gas:

0.1955 gave 0.4360 CO₂ and 0.0548 H₂O. C = 60.82; H = 3.11.

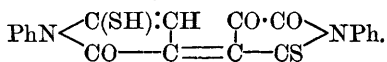
0.2396 „ 14.8 c.c. moist nitrogen at 17° and 769 mm. N = 7.25.

0.2395 „ 0.2843 BaSO₄. S = 16.30.

C₂₀H₁₂O₃N₂S₂ requires C = 61.22; H = 3.06; N = 7.14; S = 16.32 per cent.

Dithioxanthoxalanil is not attacked by hydrochloric acid even on boiling; it does not dissolve in either sodium carbonate or caustic potash at the ordinary temperature, but on digesting it with dilute alkalis (15 per cent.) it gradually dissolves and is transformed into

The Isomeride of Dithioxanthoxalanil,



This is isolated by adding dilute hydrochloric acid to the yellow alkaline solution, when it is precipitated as a red solid. After being washed with water, it is dissolved in boiling alcohol; the solution, on cooling, deposits long, red needles which do not melt, but decompose at about 195°:

0.2012 gave 0.4495 CO₂ and 0.0569 H₂C. C = 60.93; H = 3.14.

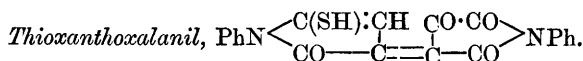
0.1970 „ 0.4420 „ „ 0.0545 „ C = 61.19; H = 3.07.

0.2302 „ 14.4 c.c. moist nitrogen at 18° and 758 mm. N = 7.20.

0.2105 „ 0.2507 BaSO₄. S = 16.35.

C₂₀H₁₂O₃N₂S₂ requires C = 61.22; H = 3.06; N = 7.14; S = 16.32 per cent.

The isomeride of dithioxanthoxalanil is moderately soluble in boiling alcohol, more readily so in hot glacial acetic acid; it dissolves in caustic potash or in sodium carbonate, yielding yellowish-red solutions.



This compound is formed on boiling dithioxanthoxalanil with aqueous caustic potash (15—20 per cent.) in a flask with a reflux condenser. It is necessary to continue the heating for some time. The transformation is complete after six hours' boiling, otherwise a mixture of thioxanthoxalanil and the tautomeride of dithioxanthoxalanil is produced. Their separation may be effected by means of boiling alcohol, in which the latter substance is fairly soluble, whereas thioxanthoxalanil is almost insoluble. The yellowish-red solution, when treated with hydrochloric acid, evolves hydrogen sulphide and yields a gelatinous precipitate which, after being washed with water is dried on porous porcelain. The substance dissolves in a large quantity of boiling glacial acetic acid, and, on cooling, crystallises in shiny, orange plates which melt and decompose at 216—218°:

0.2053 gave 0.4797 CO₂ and 0.0603 H₂O. C = 63.72 ; H = 3.26.

0.2062 „ 13.6 c.c. moist nitrogen at 18° and 746.5 mm. N = 7.48.

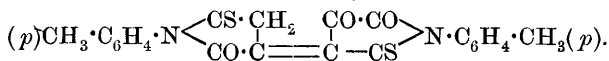
0.2460 „ 0.1510 BaSO₄. S = 8.43.

C₂₀H₁₂O₄N₂S requires C = 63.83 ; H = 3.19 ; N = 7.44 ; S = 8.51 per cent.

Thioxanthoxalanil dissolves in aqueous sodium carbonate on warming to yield a pale yellow solution, but it is insoluble in concentrated hydrochloric acid even on boiling.

The formation of this substance is not accompanied by the production of aniline and oxalic acid, and this fact indicates that a complete decomposition is not effected by the dilute alkali ; this does not take place until dithioxanthoxalanil is boiled with concentrated (about 75 per cent.) aqueous caustic potash. The brown crystals first dissolve, yielding a red solution which shortly deposits a yellow solid ; this afterwards disappears, and a green liquid is produced which retains an oil in suspension. After one hour's heating, the product of the reaction is agitated with ether ; this extracts an oil which has been recognised as aniline. The alkaline layer gives with dilute hydrochloric acid a gelatinous precipitate which dissolves in ether and, on removal of the solvent, is left behind as a green resin. The remaining acid solution contains oxalic acid.

Dithioxanthoxalo-p-toluidil,

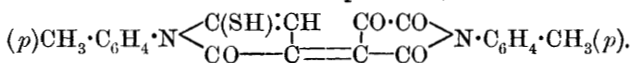


Thioaceto-*p*-toluidide, which had been prepared according to Jacobson and Ney's directions (*Ber.*, 1889, 22, 906), is not so readily soluble in benzene as thioacetanilide. On adding this substance (33 grams), dissolved in hot benzene, to the solution which is formed by mixing dry sodium ethoxide (13.6 grams) suspended in benzene, and ethyl oxalate (29.5 grams), a precipitate is formed in this case also ; this dissolves after several hours, yielding a deep red solution which, however, on standing overnight, does not deposit a solid. It is agitated with water, and the aqueous layer is treated with an excess of hydrochloric acid, when a cloudiness is produced which, after a short time, coalesces into a red solid ; this dissolves in much boiling glacial acetic acid, and, on cooling, crystallises in bunches of dark red needles which are paler in colour than dithioxanthoxalanil. The substance melts and decomposes at about 248° :

0.2020 gave 0.4645 CO₂ and 0.0708 H₂O. C = 62.71 ; H = 3.89.

0.2080 „ 11.6 c.c. moist nitrogen at 16° and 775 mm. N = 6.63.

C₂₂H₁₆O₃N₂S₂ requires C = 62.85 ; H = 3.81 ; N = 6.67 per cent.

Thioxanthoxalo-p-toluidil,

Dithioxanthoxalo-*p*-toluidil dissolves in dilute aqueous caustic potash, but not so readily as dithioxanthoxalanil; it yields a dark red solution which, on treatment with hydrochloric acid, forms a red precipitate, and at the same time hydrogen sulphide is evolved. This indicates that the formation of the isomeride of the dithio-derivative is accompanied by the production of thioxanthoxalo-*p*-toluidil. This conclusion is corroborated by the fact that the red precipitate is a mixture. I have not been able to separate it, and on analysis of the product, which had been recrystallised from alcohol, the following results were obtained:

0.2004 gave 0.4683 CO₂ and 0.0725 H₂O. C = 63.73; H = 4.01; which lie between the numbers required for the two substances:

C₂₂H₁₆O₃N₂S₂ requires C = 62.85; H = 3.81,

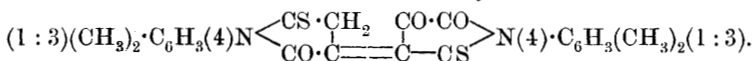
C₂₂H₁₆O₄N₂S „ C = 65.34; H = 3.96 per cent.

In order to prepare thioxanthoxalo-*p*-toluidil in a pure state, the dithio-compound is boiled with an excess of caustic potash (15–20 per cent.) for five to six hours; the alkaline solution, when cold, is mixed with dilute hydrochloric acid, when hydrogen sulphide is evolved and a yellow solid is precipitated. This, after being washed with water, is dried on a porous plate and then dissolved in boiling alcohol, in which it is only sparingly soluble; on cooling, shiny, orange plates separate which are paler in colour than the corresponding thioxanthoxalanil, and melt at 226–228° with decomposition:

0.2018 gave 0.4815 CO₂ and 0.0722 H₂O. C = 65.07; H = 3.97.

C₂₂H₁₆O₄N₂S requires C = 65.34; H = 3.96 per cent.

This substance, like thioxanthoxalanil, readily dissolves in alkalis as well as alkali carbonates.

Dithioxanthoxalo-m-xylylidil.

The solution which is formed on adding ethyl oxalate (11 grams) to sodium ethoxide (5 grams), suspended in benzene, when mixed with thioaceto-*m*-xylylidide (13 grams) dissolved in benzene (it is readily soluble in this solvent), yields a precipitate which disappears in the course of a day, forming a dark red solution. This does not deposit a

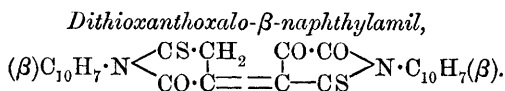
solid, but on treating the aqueous extract with hydrochloric acid an oily product is precipitated which, on standing, sets to a dark brown solid. This is more soluble in boiling glacial acetic acid than the former dithio-derivative, and, on cooling, crystallises in brick-red, prismatic plates which soften at 225° and melt at about 235° with decomposition :

0.2002 gave 0.4710 CO_2 and 0.0820 H_2O . $\text{C} = 64.16$; $\text{H} = 4.55$.

0.2270 „ 12.2 c.c. moist nitrogen at 15° and 773 mm. $\text{N} = 6.40$.

0.2587 „ 0.2722 BaSO_4 . $\text{S} = 14.45$.

$\text{C}_{24}\text{H}_{20}\text{O}_3\text{N}_2\text{S}_2$ requires $\text{C} = 64.28$; $\text{H} = 4.46$; $\text{N} = 6.25$; $\text{S} = 14.29$ per cent.



This substance is formed in the same way as the former dithio-compound, using β -naphthylthioacetamide. In order to dissolve the amide, a large quantity of hot benzene is required; the precipitate obtained on adding this solution to the mixture of sodium ethoxide and ethyl oxalate gradually dissolves, and the solution, in the course of a day, deposits a red solid which is soluble in water. On adding hydrochloric acid to the aqueous layer, a red precipitate is formed which is insoluble in alcohol or glacial acetic acid, but dissolves in boiling nitrobenzene and, on cooling, crystallises in small red needles. These are separated from the dark coloured mother liquor by filtration and frequently washed with boiling alcohol. The substance does not melt, but begins to darken at about 250° and finally turns black :

0.2020 gave 0.5065 CO_2 and 0.0625 H_2O . $\text{C} = 68.38$; $\text{H} = 3.43$.

0.2123 „ 10.4 c.c. moist nitrogen at 19° and 770 mm. $\text{N} = 5.70$

$\text{C}_{28}\text{H}_{16}\text{O}_3\text{N}_2\text{S}_2$ requires $\text{C} = 68.29$; $\text{H} = 3.25$; $\text{N} = 5.69$ per cent.

This compound reacts with caustic potash in the same way as the dithio-derivatives. On boiling with the alkali (15 per cent.), it dissolves with the exception of a small quantity of a black solid; the dark colour of the solution then changes to yellowish-red. After four hours' heating, the solution is poured off from the solid which adheres to the sides of the flask and treated with dilute hydrochloric acid, when hydrogen sulphide is evolved and a red precipitate is formed. This is insoluble in alcohol or glacial acetic acid; it dissolves in boiling nitrobenzene, but is decomposed at the same time, and the solution, on cooling, does not deposit any solid. I have not analysed this substance, but there cannot be any doubt that it is thioxanthoxalo- β -naphthylamil.

Reduction of Dithioxanthoxalanil.

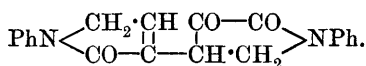
The dark red solution of dithioxanthoxalanil in glacial acetic acid is rapidly decolorised by zinc dust. Instead of bringing the dithio-compound into solution, which requires a considerable volume of the solvent, it is more convenient to boil the substance (8 grams) with a smaller quantity of glacial acetic acid (about 500 c.c.), and to add gradually an excess of zinc dust to the suspension, when in a few minutes the action is complete. The product is filtered while hot through asbestos, and the residue again extracted with acetic acid. The filtrate, which has a pale yellow colour, cannot be concentrated by distillation of the acid, because it turns red; it is therefore mixed with water, when a gelatinous substance is precipitated. This is washed with water, dried on a porous plate, and dissolved in boiling glacial acetic acid; the solution, on cooling, deposits grey, shiny plates which do not melt, but begin to darken at about 240° and finally turn black:

0.2015 gave 0.5330 CO_2 and 0.0885 H_2O . $\text{C} = 72.14$; $\text{H} = 4.88$.

0.2160 „ 15.8 c.c. moist nitrogen at 18° and 768 mm. $\text{N} = 8.53$.

$\text{C}_{20}\text{H}_{16}\text{O}_3\text{N}_2$ requires $\text{C} = 72.30$; $\text{H} = 4.82$; $\text{N} = 8.43$ per cent.

The substance is insoluble in benzene, sparingly soluble in hot alcohol, more readily so, however, in boiling glacial acetic acid. Its constitution, as stated before (p. 799), is probably to be represented thus:



A similar compound is formed from dithioxanthoxalo-*p*-toluidil, which crystallises from glacial acetic acid in nearly colourless prisms, and on heating behaves like the former substance. The yield in both cases is very small.

The compound, $\text{C}_{20}\text{H}_{16}\text{O}_3\text{N}_2$, which is produced on reduction of dithioxanthoxalanil (and the corresponding substance obtained from the homologue of the dithio-derivative) is not soluble either in sodium carbonate or caustic soda at the ordinary temperature, but on boiling with these reagents yields a blue substance; this, in the presence of alkali, is sparingly soluble in water; it dissolves, however, fairly readily when the alkali has been washed away. The blue solid and its solution, on treatment with hydrochloric acid, turn red, and yield a compound which by alkalis is transformed back again into its blue salts. The red substance is insoluble in alcohol or glacial acetic acid, but dissolves in hot nitrobenzene, and on cooling separates in reddish-brown crystals. The small yield of the reduction product of dithio-

xanthoxalanil has prevented me from studying more closely the remarkable transformation it undergoes when treated with alkalis, but I am continuing this investigation in order to prove the relation of the substance which is thus formed to the compounds with similar properties.

GONVILLE AND CAIUS COLLEGE,
CAMBRIDGE.
