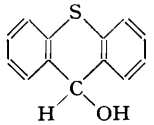
163. *Xanthones and Thioxanthones. Part II. Derivatives of Thioxanthhydrol, 9-Xanthylamine, and 9-Thioxanthylamine.*

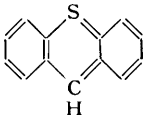
By Frederick G. Mann and J. Hedley Turnbull.

2- and 3-(2-Diethylaminoethylamino)thioxanthones and also their 7-chloro- and 7-methyl derivatives have been reduced to the corresponding hydrols, and the latter in turn converted into their perchlorate hydrogen perchlorate salts, (V) and (VI). The two isomeric series of salts are entirely different in properties, the 2-substituted compounds forming blue-black crystals which hydrolyse in water, whilst the 3-substituted compounds form stable crimson crystals. In each series the corresponding chlorozincates are similar in appearance and properties to the perchlorates. The reason for this marked difference between the two series is discussed.

9-Xanthylamine and di-9-xanthylamine, and their thio-analogues, have been synthesised. They undergo very ready hydrolysis by acids, even at room temperature, with loss of ammonia, and synthetic work on their derivatives was therefore discontinued.

It is known that thioxanthone, like xanthone itself, can be reduced to the corresponding hydrol (I). The thioxanthhydrol thus produced acts as a weak base, and with acids gives rise to salts in which the cation must have a resonance structure to which the sulphonium form (II) and carbonium forms, such as (III) and (IV), contribute. Of these, the major contribution is


(I.)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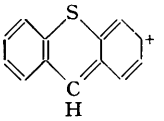
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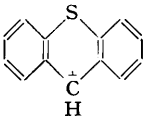
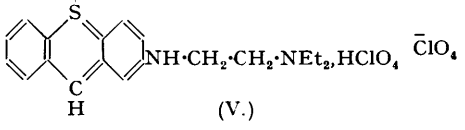

(IV.)

probably made by the sulphonium form (II), for the " aromatic " structure of the central ring would give enhanced stability to this form. Nevertheless, salts of both xanthhydrol and thioxanthhydrol undergo ready dissociation in water (Werner, *Ber.*, 1901, **34**, 3302; Hilditch and Smiles, *J.*, 1911, **99**, 157; *cf.* also Gomberg and Cone, *Annalen*, 1910, **376**, 188; Kehrmann, *Annalen*, 1910, **372**, 307).

We have studied in some detail the reduction products of the 2- and 3-(2-diethylaminoethylamino)thioxanthones described in the previous paper. The former on reduction gave the corresponding thioxanthhydrol as an unstable gum which, however, on treatment with perchloric acid gave the crystalline perchlorate hydrogen perchlorate of composition (V). In this salt the hydrogen perchlorate undoubtedly neutralises the terminal tertiary group; the latter is normally more strongly basic than the secondary amine group, which moreover in compounds of this type must be largely inactivated by the resonance of the molecule; the perchlorate ion neutralises the normal thioxanthylium ion. It will be seen that this salt would show canonical forms similar in type to (II), (III), and (IV) and should therefore have similar properties to the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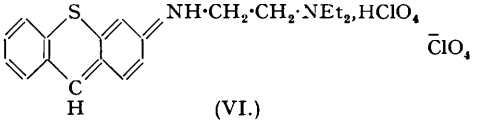

(VI.)

simple thioxanthylium salts. This has proved to be the case. We find that (V) and its 7-chloro-derivative form blue-black crystals which are readily hydrolysed by water, and the colour of their solutions in acetic acid slowly fades at room temperature. The first hydrol also gave an analogous chlorozincate, $XCl,HZnCl_3$ where X represents the cation of (V); this also formed blue-black crystals having similar physical properties to those of the perchlorates.

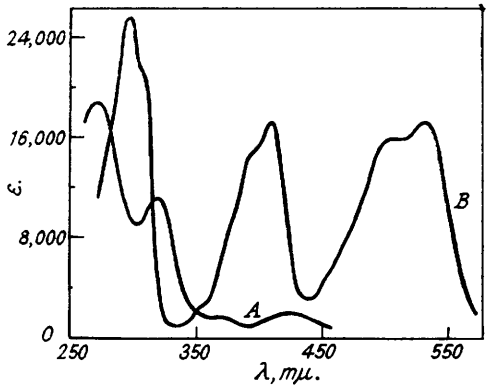
The 3-(2-diethylaminoethylamino)thioxanthones underwent similar reduction to give the hydrols, and the perchlorate hydrogen perchlorate salts had a similar composition (VI) to the 2-substituted analogues. Their properties were entirely different, however, for the 3-substituted salts formed crimson needles which were soluble in water without apparent hydrolysis; they

gave red solutions in glacial acetic acid which showed no fading after several days at room temperature. These crimson needles were furnished by the parent compound (VI) and by its 7-chloro- and 7-methyl derivative. All three cations furnished crimson chlorozincates, $XCl,HZnCl_3$, which had precisely analogous physical properties.

There is little doubt that the different colour and the greater stability of the 3-substituted salts arise from the greater degree of resonance which they can show. It will be clear that the resonance hybrid of these compounds will receive contributions not only from the canonical forms corresponding to (II), (III), and (IV), but also (and probably markedly) from the form (VI), and hence will be more stable than the 2-substituted analogues. This wider basis of resonance is confirmed by the absorption spectra (*A*) and (*B*) of the salts (V) and (VI), respectively. The curve (*A*) shows pronounced absorption in the ultra-violet and weak absorption in the visible region. In contrast the curve (*B*) shows a greater intensity of absorption, the bands are displaced to longer wave-lengths, and absorption in the visible region is strong.

These perchlorates and chlorozincates are thus in marked contrast to the chlorozincates of the unreduced 2- and 3-(diethylaminoethylamino)-xanthones and -thioxanthones, in which resonance of the above type is absent and in which therefore both amine groups can show their normal basic properties, so that the compounds form, for example, normal dihydrochlorides (see preceding paper).

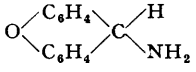
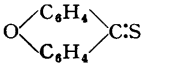
The preparation of 9-xanthylamine (VII) and of 9-thioxanthylamine, which are structurally akin to the corresponding hydrols, has received little attention in the past. We have investi-



(*A*) *Absorption spectrum of compound* (V) *in acetic acid.*
(*B*) ,, ,, ,, (VI) ,, ,,

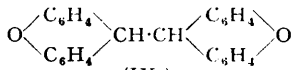
gated their synthesis in the hope that subsequent condensation with, for example, 2-diethylaminoethyl chloride would give the 2-diethylaminoethylamino side-chain in the 9-position. All previous compounds prepared in this investigation have had this side-chain in the same general plane as the tricyclic system; the new compounds would be fundamentally different in that the side-chain would be at right angles to this plane, and a correspondingly fundamental difference in therapeutic properties might possibly result.

Treatment of xanthone or xanthione (VIII) with formamide (Leuckhart reaction) left these compounds unchanged, and the reduction of xanthone oxime was therefore investigated.

(VII.)   (VIII.)

This oxime cannot apparently be prepared directly by the action of hydroxylamine on xanthone (Fosse, *Compt. rend.*, 1906, **143**, 749), although Graebe and Röder (*Ber.*, 1899, **32**, 1678) record its preparation from xanthone anil. We find, however, that it can readily be prepared by the action of hydroxylamine on xanthione (VIII). Reduction of the oxime with zinc and acetic acid furnished only di-9-xanthyl (IX); reduction with sodium in ethanolic solution gave however the desired xanthylamine (VII) which was isolated as its acetate. The amine was also characterised by acetylation to *N*-9-xanthylacetamide, which Fosse (*loc. cit.*) had prepared by the interaction of xanthhydrol and acetamide, but had failed to hydrolyse to the xanthylamine. We have found the acetyl compound to be very resistant to alkaline hydrolysis, but it readily loses ammonia with acids.

9-Xanthylamine forms a well-defined crystalline hydrochloride, acetate, and picrate. It is however extremely susceptible to acid hydrolysis, and aqueous solutions of its salts slowly decompose at room temperature, and rapidly on being warmed, to give ammonia and a mixture of xanthhydrol and di-9-xanthyl ether (X). Even the picrate in warm ethanolic solution



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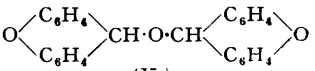
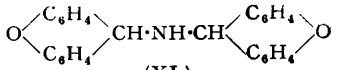


(X.)

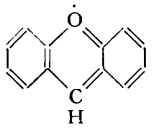


(XI.)

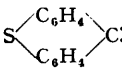
rapidly gives ammonium picrate, whilst the hydrochloride when dissolved in concentrated hydrochloric acid gives xanthylium chloride.

Di-9-xanthylamine (XI) was prepared by the action of ammonia in ether on xanthylium chloride ferrichloride (XII). It is a crystalline compound, very susceptible to acid hydrolysis, and solutions in dilute hydrochloric or acetic acids consequently become milky.

(XII.)



$\bar{Cl},FeCl_3$



(XIII.)

We have attempted to prepare 9-thioxanthylamine (as VII) by converting thioxanthione (XIII) into thioxanthone oxime, and reducing the latter with sodium and ethanol, but the isolation of the pure amine by this method was difficult. When however thioxanthylium chloride ferrichloride (as XII) was treated with ammonia, both 9-thioxanthylamine and di-9-thioxanthylamine (as XI) were isolated. Both gave crystalline salts which underwent rapid hydrolysis with acids.

In view of the instability of all these amino-derivatives, the investigation of their condensation with alkyl halides was discontinued.

Experimental.

2-(2-*Diethylaminoethylamino*)*thioxanthylium Perchlorate Hydrogen Perchlorate.* (V).—2-(2-Diethylaminoethylamino)thioxanthone (0·2 g.) in ethanol (10 c.c.) was mixed with a solution of sodium hydroxide (0·6 g.) in water (0·5 c.c.), stirred under reflux on the water-bath, and zinc dust (0·25 g.) added in small portions during 15 minutes. 15 Minutes later the hot mixture was filtered, cooled, and diluted with water, and the resultant suspension extracted with ether. The ethereal extracts were washed with sodium hydroxide solution and dried (K_2CO_3), and the ether removed. The residual gum was dissolved in cold glacial acetic acid (10 c.c.), the green solution filtered, and a mixture of glacial acetic acid (40 c.c.) and 30% aqueous perchloric acid (0·6 c.c.) gradually added. The solution became Prussian blue, and the *perchlorate* separated as a blue-black crystalline powder (0·18 g.), m. p. 175° (decomp.) sintering at 160° (Found : C, 44·8; H, 4·4; N, 5·15. $C_{19}H_{23}N_2S,ClO_4,HClO_4$ requires C, 44·6; H, 4·7; N, 5·5%).

7-*Chloro*-2-(2-*diethylaminoethylamino*)*thioxanthylium Perchlorate Hydrogen Perchlorate.*—7-Chloro-2-(2-diethylaminoethylamino)thioxanthone (0·2 g.) was reduced and converted into the *perchlorate* exactly as in the foregoing experiment : it separated as a blue-black crystalline powder (0·19 g.), m. p. 180° (decomp.) sintering at 170° (Found : C, 42·0; H, 4·2; N, 5·3. $C_{19}H_{22}N_2ClS,ClO_4,HClO_4$ requires C, 41·8; H, 4·2; N, 5·1%).

2-(2-*Diethylaminoethylamino*)*thioxanthylium Chlorozincate.*—2-(2-Diethylaminoethylamino)thioxanthone (0·2 g.) was reduced as before. The residual gum was dissolved in glacial acetic acid (5 c.c.) and a 4% solution of zinc chloride in concentrated hydrochloric acid (2 c.c.) added, whereupon the grass-green solution became Prussian blue, and the *chlorozincate* separated as a metallic blue-black crystalline powder (0·21 g.), m. p. 190° (decomp.) (Found : C, 44·1; H, 4·45; N, 5·7. $C_{19}H_{23}N_2ClS,HZnCl_3$ requires C, 43·9; H, 4·7; N, 5·4%).

3-(2-*Diethylaminoethylamino*)*thioxanthylium Perchlorate Hydrogen Perchlorate* (VI).—3-(2-Diethylaminoethylamino)thioxanthone (0·2 g.) was reduced as in the foregoing experiments. The gummy product was isolated by extraction with ether and dissolved in glacial acetic acid (10 c.c.), the red solution filtered, and a solution of 30% perchloric acid (0·7 c.c.) in glacial acetic acid (60 c.c.) added. The monohydrated *perchlorate* slowly crystallised as a bright red powder, which was rapidly recrystallised from glacial acetic acid, giving glistening crimson plates (0·14 g.), m. p. 134—136° (sintering 130°) (Found : C, 43·6 H, 4·9; N, 5·4; Cl, 13·1; S, 6·2. $C_{19}H_{23}N_2S,ClO_4,HClO_4,H_2O$ requires C, 43·1; H, 5·0; N, 5·3; Cl, 13·4; S, 6·1%).

3-(2-*Diethylaminoethylamino*)-7-*methylthioxanthylium Perchlorate Hydrogen Perchlorate.*—3-(2-Diethylaminoethylamino)-7-methylthioxanthone (0·2 g.) was reduced as before, and the *perchlorate*, isolated in a similar way to the previous salt, separated as a crystalline scarlet powder (0·18 g.), m. p. 115° (decomp.) (Found : C, 45·9; H, 5·0; N, 5·55. $C_{20}H_{25}N_2S,ClO_4,HClO_4$ requires C, 45·7; H, 5·0; N, 5·3%).

7-*Chloro*-3-(2-*diethylaminoethylamino*)*thioxanthylium Perchlorate Hydrogen Perchlorate.*—7-Chloro-3-(2-diethylaminoethylamino)thioxanthone (0·2 g.), reduced and then treated as before, gave the *perchlorate*

as a scarlet powder (0·21 g.), m. p. 232 (decomp.) (Found: C, 42·2; H, 4·4; N, 5·2. $C_{19}H_{22}N_2ClS,ClO_4,HClO_4$ requires C, 41·8; H, 4·2; N, 5·1%).

3-(2-*Diethylaminoethylamino*)*thioxanthylium Chlorozincate*.—3-(2-Diethylaminoethylamino)thioxanthone (0·2 g.) in ethanol (10 c.c.) was reduced as in the foregoing experiment. The mixture was filtered, and a 2% solution of zinc chloride in dilute hydrochloric acid (20 c.c.) added. The red solid, m. p. 215—218° (0·27 g.), which separated was recrystallised from a 2% solution of zinc chloride in dilute hydrochloric acid and gave lustrous crimson needles (0·22 g.) of the *chlorozincate*, m. p. 230° (decomp.) (Found: C, 44·3; H, 4·9; N, 5·4; S, 6·3; Cl, 26·6. $C_{19}H_{23}N_2ClS,HZnCl_3$ requires C, 43·9; H, 4·7; N, 5·4; S, 6·2; Cl, 27·3%).

3-(2-*Diethylaminoethylamino*)-7-*methylthioxanthylium Chlorozincate*.—3-(2-Diethylaminoethylamino)-7-methylthioxanthone (0·2 g.) was reduced as before, and the *chlorozincate*, when similarly recrystallised, separated as crimson needles (0·2 g.), m. p. 238—240° (Found: C, 44·8; H, 5·25; N, 5·35. $C_{20}H_{25}N_2ClS,HZnCl_3$ requires C, 45·0; H, 4·9; N, 5·3%).

7-*Chloro*-3-(2-*diethylaminoethylamino*)*thioxanthylium Chlorozincate*.—7-Chloro-3-(2-diethylaminoethylamino)thioxanthone on reduction as before afforded the *chlorozincate*, which after the usual recrystallisation separated as scarlet needles, m. p. 234—235° (decomp.) (Found: C, 40·6; H, 4·5; N, 4·9. $C_{19}H_{22}N_2Cl_2S,HZnCl_3$ requires C, 41·1; H, 4·2; N, 5·1%).

Thiolacetic Acid.—The acid, prepared by Clarke and Hartman's method (*J. Amer. Chem. Soc.*, 1924, **46**, 1731), and carefully fractionated through a long column, was obtained as a colourless, highly refracting liquid (b. p. 90—92°) with a pungent unpleasant smell. The iodine equivalent (ε) of the product was determined by Klason and Carlson's method (*Ber.*, 1906, **39**, 738) (Found: ε, 87. Calc.: ε, 76).

Xanthione.—Xanthone (15 g.) and thionyl chloride (15 c.c.) were heated on a water-bath for 4 hours. The clear red solution was evaporated to dryness in a vacuum, the residue dissolved in dry benzene (90 c.c.) and cooled, and thiolacetic acid (22·5 g.) added dropwise in a stream of nitrogen. The dark-brown product was heated on the water-bath for 4 hours, the solution evaporated to half-bulk and cooled, and the solid collected and then recrystallised from benzene giving xanthione as deep-red needles (7·5 g.), m. p. 152—154°. Schönberg (*Ber.*, 1928, **61**, 1382) records m. p. 156°.

Xanthone Oxime.—Finely powdered hydroxylamine hydrochloride (2·5 g.) was added in small portions to a solution of xanthione (2·5 g.) in warm dry pyridine (25 c.c.). The dark-green solution was heated at 100° for 2 hours; the colour faded and hydrogen sulphide was evolved. The product was cooled and poured into water, and the oxime separated as an oil which rapidly solidified (2·35 g.); recrystallisation from benzene gave glistening white needles, m. p. 160—161° (Found: C, 74·2; H, 4·3; N, 6·5. Calc. for $C_{13}H_9O_2N$: C, 73·9; H, 4·3; N, 6·6%). Graebe and Röder (*loc. cit.*) record m. p. 164°.

The oxime was soluble in concentrated hydrochloric acid, but insoluble in dilute aqueous sodium hydroxide. A solution in concentrated sulphuric acid was colourless, and showed no fluorescence.

Reduction of Xanthone Oxime with Zinc in Acetic Acid.—Xanthone oxime (1·5 g.) was stirred under reflux with glacial acetic acid (20 c.c.) and water (1 c.c.), and zinc dust (3·5 g.) added during 15 minutes. The solution became brown, and a white crystalline solid separated. The mixture was heated under reflux for 1 hour and cooled, and the solid collected and extracted with ethyl acetate (Soxhlet). The extracts were evaporated to dryness, and the residue (0·9 g.) recrystallised from glacial acetic acid giving long white needles, m. p. 204—205°, identical with di-9-xanthyl prepared by the reduction of xanthhydrol (Wanscheidt and Moldavski, *Ber.*, 1930, **63**, 1368).

9-*Xanthylamine Acetate*.—Xanthone oxime (1·0 g.) was heated under reflux with alcohol (40 c.c.) whilst sodium (4·0 g.; small shavings) was added during 20 minutes. The product was cooled, ice added, and the mixture extracted with ether. The ethereal solution was washed with water, and shaken with cold 10% acetic acid (2 × 5 c.c.). The united acid extracts were cooled to 0° and scratched to induce crystallisation; the *amine acetate* separated as a white solid (0·5 g.), m. p. 150—151° (decomp.). A portion, recrystallised from benzene (containing a trace of acetic acid), gave white needles (Found: C, 69·5; H, 5·8; N, 5·5. $C_{13}H_{11}ON,C_2H_4O_2$ requires C, 70·0; H, 5·9; N, 5·5%).

The *amine picrate*, prepared by adding ethanolic picric acid to a solution of the acetate (0·1 g.) in ethanol (3 c.c.), separated in yellow needles, m. p. 200—202° (Found: C, 53·7; H, 3·5; N, 13·4. $C_{13}H_{11}ON,C_6H_3O_7N_3$ requires C, 53·5; H, 3·3; N, 13·1%).

A hot ethanolic solution of the picrate slowly deposited yellow crystals, m. p. 290° (decomp.), which showed no depression of m. p. on admixture with authentic ammonium picrate (Found: C, 30·1; H, 2·5; N, 23·2. Calc. for $C_6H_6O_7N_4$: C, 29·3; H, 2·5; N, 22·8%).

9-*Xanthylamine*.—Dilute ammonia solution was added to a suspension of 9-xanthylamine acetate (0·16 g.) in water (5 c.c.). The *base* separated as an oil which slowly solidified and, when recrystallised from petroleum (b. p. 40—60°), gave long white needles, m. p. 59—61° (Found: C, 79·6; H, 5·6; N, 6·9. $C_{13}H_{11}ON$ requires C, 79·2; H, 5·6; N, 7·1%). A solution in concentrated sulphuric acid was yellow with an intense-green fluorescence.

The *hydrochloride*, prepared by adding cold saturated alcoholic hydrogen chloride (1 c.c.) to an ice-cold solution of the base (0·1 g.) in ethanol (1·5 c.c.), separated as white needles (0·07 g.), m. p. 355° (decomp.) (Found: C, 67·3; H, 5·6; N, 6·1. $C_{13}H_{11}ON,HCl$ requires C, 66·8; H, 5·2; N, 6·0%). A solution of the hydrochloride (0·2 g.) in cold water (5 c.c.) was gently warmed to 100°; a white crystalline solid (0·15 g.), m. p. 135—145°, separated. It contained no nitrogen, and was evidently impure di-9-xanthyl ether (Found: C, 82·9; H, 5·1. Calc. for $C_{26}H_{18}O_3$: C, 82·5; H, 4·8%).

N-9-*Xanthylacetamide*.—Xanthylamine (0·1 g.) and acetic anhydride (0·1 g.) were heated at 100° for 30 minutes. The product was cooled and diluted with water, and the solid was collected and recrystallised from 80% dioxan–water giving long white needles, m. p. 240—242° undepressed on admixture with

authentic *N*-9-xanthylacetamide prepared from xanthhydrol (Fosse, *loc. cit.*; Phillips and Pitt, *J. Amer. Chem. Soc.*, 1943, **65**, 1355).

Xanthylium Chloride Ferrichloride (XII).— Xanthhydrol (1·0 g.) was dissolved in dry ether (10 c.c.), saturated with dry hydrogen chloride at 0°, and an ethereal solution of anhydrous ferric chloride (1 g.) added. The double salt was precipitated as a yellow solid which was collected, washed with ether, and dried in a vacuum; it (0·8 g.) had m. p. 190° (sintering at 185°). Gomberg and Cone (*loc. cit.*) record m. p. 193°.

Di-9-xanthylamine.—A suspension of the ferrichloride (2·0 g.) in ether (30 c.c.) was saturated with dry ammonia at 0°. The filtered product was evaporated, leaving a gum which crystallised on treatment with petroleum to give *di-9-xanthylamine* (0·22 g.); crystallisation from ethanol afforded glistening needles, m. p. 154° (Found: C, 82·7; H, 5·3; N, 4·2. $C_{26}H_{19}O_2N$ requires C, 82·7; H, 5·1; N, 3·7%). A solution of the base in concentrated sulphuric acid was yellow and showed an intense green fluorescence.

Thioxanthone.—This compound was prepared by the action of concentrated sulphuric acid on a suspension of *o*-mercaptobenzoic acid in benzene (Davis and Smiles, *J.*, 1910, **97**, 1296).

Thioxanthione.—Thioxanthone (9·3 g.) and thionyl chloride (9·3 c.c.) were heated on a water-bath for 4 hours. The clear dark-red solution was evaporated to dryness in a vacuum, the residue dissolved in dry benzene (130 c.c.), and thiolacetic acid (16·3 g.) dropped in at 0°, under a nitrogen atmosphere. The product was heated on the water-bath for 5 hours, filtered, and evaporated to small bulk, whereupon the thioketone was slowly deposited as a lustrous brown solid (6·9 g.), m. p. 160—168°. Schönberg (*loc. cit.*) records m. p. 168°.

Thioxanthone Oxime.—The crude thioxanthione (6·9 g.) was dissolved in warm pyridine (70 c.c.), cooled, and powdered hydroxylamine hydrochloride (7 g.) gradually added. The mixture was warmed on the water-bath for 1 hour, cooled, and poured into water, and the solid (7·7 g.) collected. The dry material was ground in a mortar with ethanol (100 c.c.) and filtered, and the filtrate diluted with water; the *oxime* was precipitated as a white solid which crystallised from petroleum (b. p. 80—100°) in pale-yellow needles (2·5 g.), m. p. 194—196° (sintering at 180°) (Found: C, 68·7; H, 4·3; N, 6·1. $C_{13}H_9ONS$ requires C, 68·7; H, 4·0; N, 6·2%). A solution of the oxime in concentrated sulphuric acid was yellow and non-fluorescent.

Thioxanthhydrol.—Thioxanthone (5 g.) suspended in ethanol (35 c.c.) was reduced by shaking with sodium amalgam exactly as in the preparation of xanthhydrol (*Org. Synth.*, Coll. Vol. I, p. 554). The hydrol was isolated as a white solid (4·2 g.), m. p. 100—102°. Hilditch and Smiles (*loc. cit.*) record m. p. 103—104°.

Thioxanthylium Chloride Ferrichloride.—This was prepared precisely as the xanthylium analogue and obtained as an orange-red solid, which was washed with ether and dried in a vacuum; it (6·5 g.) had m. p. 192—195°. Hilditch and Smiles (*loc. cit.*) record m. p. 193—194°.

Di-9-thioxanthylamine.—The above salt (6·5 g.) was suspended in ether (200 c.c.), and saturated with dry ammonia at 0°. The mixture was filtered and the ethereal filtrate concentrated to *ca.* 10 c.c., whereupon the *amine* (1·1 g.) was deposited; it separated from ethanol in crystals, m. p. 167—168° (Found: C, 76·5; H, 4·6; N, 3·5. $C_{26}H_{19}NS_2$ requires C, 76·2; H, 4·7; N, 3·4%). A solution in concentrated sulphuric acid was faintly pink, and showed a strong yellow fluorescence.

9-*Thioxanthylamine Acetate.*—Evaporation of the ethereal mother-liquors, after removal of the secondary amine in the foregoing experiment, yielded a gum (1·0 g.) which solidified on treatment with 10% acetic acid at 0° to give *thioxanthylamine acetate* (0·7 g.) which crystallised from benzene (containing a trace of acetic acid) as small white needles, m. p. 152° (sinters at 135°) (Found: C, 65·9; H, 5·6; N, 5·15. $C_{13}H_{11}NS,C_2H_4O_2$ requires C, 65·9; H, 5·55; N, 5·1%).

An aqueous solution of the salt rapidly became turbid when warmed. With concentrated sulphuric acid the salt gave a similar colour reaction to the corresponding secondary amine.

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