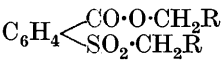
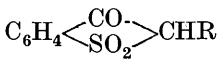
LVI.—*Derivatives of 3-Keto-2 : 3-dihydrothionaphthen 1 : 1-Dioxide.*

By AARON COHEN and SAMUEL SMILES.

CERTAIN members of this group were required in connexion with other experiments, but no systematic method of obtaining them was available. Treatment of 3-keto-2 : 3-dihydrothionaphthen with hydrogen peroxide gives the parent substance (II, R = H) in poor yield (Lanfry, *Compt. rend.*, 1912, **154**, 1517), but the method is untrustworthy for the preparation of derivatives. Price and Smiles (J., 1928, 2860) prepared 3-keto-2-*p*-nitrophenyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide (II, R = *p*-$NO_2 \cdot C_6H_4$) from the sulphone ester (I, R = *p*-$NO_2 \cdot C_6H_4$) derived from *o*-carboxybenzenesulphinic acid, and the carbethoxy-derivative (II, R = CO_2Et) was obtained in a similar manner.



(I.)



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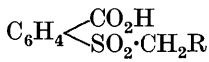


(III.)

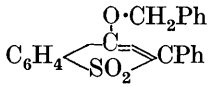
This mode of synthesis has now been further studied and, with certain limitations, has been found satisfactory; for instance, the *phenyl*, o-*nitrophenyl*, *acetyl*, and *benzoyl* derivatives (II, R = substituent) are readily obtained by reaction of the corresponding sulphone esters with sodium ethoxide.

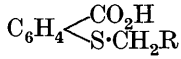
The requisite sulphone esters (I) are often conveniently obtained in one operation from an alkali *o*-carboxybenzenesulphinate and the halogen derivative, but in cases (*e.g.*, I, R = Ph) where esterification does not proceed easily under the conditions it is more convenient to treat the ethyl ester of the sulphone acid (III) with sodium ethoxide,

admixture of the product with the ether (*e.g.*, IV) thus being avoided.

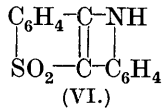
The structural conditions necessary to this closing of the ring are provided by the sulphone group (compare Troeger and Kroseberg, *J. pr. Chem.*, 1913, **87**, 67) and by the nature of R. For instance, in contrast with the corresponding sulphones, the ester of the benzyl sulphide (V, R = Ph) does not yield the ketodihydrothionaphthen with sodium ethoxide (Apitzsch, *Ber.*, 1913, **46**, 3092), the ester of *o*-carboxyphenylmethylsulphone (I, R = H) does not give the cyclic sulphone, and the *ethyl* ester of *ethylene di-o-carboxyphenylsulphone* (as III, R = CH_2·) is not converted into the dicyclic sulphone by this method.

The stability conferred on the thionaphthen ring by the substituents phenyl, acetyl, benzoyl, and nitrophenyl is remarkable; the derivatives having these substituents in the 2-position dissolve in warm aqueous alkali hydroxide without fission, whereas the parent substance is attacked by the cold reagent, yielding *o*-carboxyphenylmethylsulphone.

(IV.) 

 (V.)

Very stable polycyclic systems are easily formed from derivatives of type (II): reduction of the *o*-nitrophenyl derivative leads directly to the *thionaphthindole dioxide* (VI), and the monophenyl-



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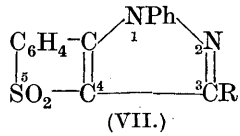
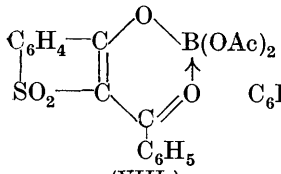


(VII.)

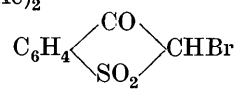
hydrazones of the acetyl and benzoyl derivatives yield the thionaphthapyrazole dioxides (VII, R = Me and Ph, respectively).

The characters of 3-keto-2-benzoyl-2 : 3-dihydrothionaphthen and of the corresponding dioxide (II, R = COPh) have been contrasted in a few typical experiments: these indicate that the latter substance approaches more closely to the β-diketonic structure than the former, which behaves as a 2-hydroxy-ketone. For example, the thionaphthen is easily acetylated and yields only a monophenylhydrazone (Hart and Smiles, J., 1924, **125**, 876), but the corresponding dioxide gives a *diphenylhydrazone* and cannot be acetylated under comparable conditions. The relationship is also well illustrated by the instability of the *borodiacetate* of the dioxide (VIII) in comparison with the stability of the characteristic *derivative* (VIII with S in place of SO_2) of the thionaphthen. This relationship accords with

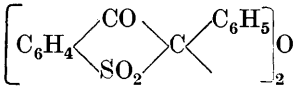
the observations of McClelland (J., 1929, 1590) that sulphur in the ortho-position to carbonyl favours enolisation of the latter by



(VIII.)



(IX.)



(X.)

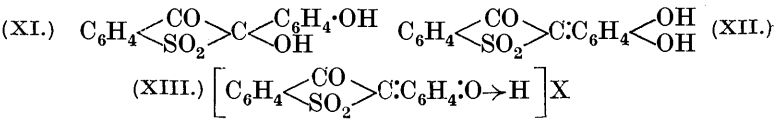
increasing the negative character of the oxygen, whereas conversion of the sulphide into the sulphone lessens the activity of the sulphur as a source of electrons and thus moderates the enolic tendency of the carbonyl oxygen.

The halogen derivatives of this series exhibit interesting features. Bromination proceeds easily at the 2-position when available hydrogen is present. The parent substance (II, R = H) yielded the 2 : 2-*dibromo*-derivative, and the *monobromo*-derivative (IX) could be obtained only by decomposition of the unstable 2-bromo-2-carbethoxy-compound (IX with CO_2Et in place of H); other bromine derivatives of the 2-substituted ring (II with Br in place of H) were more stable.

In accordance with the known character of the sulphone group and with the observations of Macbeth and his co-workers (J., 1922, **121**, 892, 904, 1116) on substances of analogous type, the halogen in the 2-bromo-derivatives is removed as hypobromite by alkali hydroxide, being replaced by hydrogen, except in the mono- and di-bromo-compounds, where the process is modified by fission of the sulphone ring system. Moreover, in the monobromo-derivatives (IX, and II with Br in place of H) the halogen quantitatively liberates iodine from potassium iodide. These reactions appear to be characteristic of chlorine or bromine in the 2-position. Nitrous acid also attacks hydrogen in this position: in the parent substance replacement is complete, the nitroso-derivative undergoing further substitution (compare Friedländer, *Ber.*, 1908, **41**, 227), but with the 2-phenyl derivative oxidation ensues, the *oxide* (X) being formed. This oxide is devoid of basic character and the corresponding 2-bromo-derivatives do not exhibit the properties of salts.

These facts give useful information concerning the structure of the product obtained by the action of excess of nitrous acid on the 2-*p*-aminophenyl derivative. The red crystalline material thus formed is basic in character and the chloride, from which the base is regenerated by hydrolysis, furnishes a *ferrichloride* and a *chloroplatinate*. In composition the base conforms with the structure (XI), but this arrangement, which involves the association of

hydroxyl with the 2-carbon atom, cannot be adopted, since the 2-oxide is entirely lacking in basic character. Similarly, the association of halogen with the 2-position of the thionaphthen nucleus (XI with Cl in place of OH) cannot be admitted in the case of the chloride or bromide; these salts are merely hydrolysed by water or



dilute alkalis and do not exhibit the characteristic behaviour of the 2-bromo-derivatives (IX, and II with Br in place of H), which liberate hypobromite on treatment with such agents. Moreover, a quinolide structure (XII) similar to that proposed by Gomberg (*J. Amer. Chem. Soc.*, 1913, **35**, 1035) for one of the isomeric forms of 4-hydroxytriphenylcarbinol and analogous substances is unacceptable, since removal of water from the base in question is effected only with difficulty, prolonged heating in a vacuum in presence of phosphoric oxide being necessary. On the other hand, the formation and properties of the base and salts are well expressed by the formula XIII (X = OH or Cl) in which the kation is formed by co-ordination of hydrogen with the carbonyl group of the quinone. This view accords with those of Pfeiffer (*e.g.*, *Annalen*, 1917, **413**, 328) on the nature of salts formed by substances containing the carbonyl group.

EXPERIMENTAL.

3-Keto-2-benzoyl-2 : 3-dihydrothionaphthen 1 : 1-Dioxide (II, R = COPh).—(*a*) A concentrated solution of ω-bromoacetophenone (23 g.) was added to an alcoholic solution of *o*-carboxybenzenesulphinic acid (10 g.) (J., 1928, 2860) which had been neutralised with concentrated aqueous potassium hydroxide. When the mixture was boiled, potassium bromide separated (½ hour); the cooled liquid yielded a further quantity of this salt together with *phenacyl-o-carbophenacylphenylsulphone* (I, R = COPh). This substance (70% yield) separated from acetone–alcohol in needles, m. p. 164° (Found: C, 65·1; H, 4·5; S, 7·5. $C_{23}H_{18}O_6S$ requires C, 65·4; H, 4·3; S, 7·6%). A solution of this ester (8 g.) in alcohol (50 c.c.) in which sodium (0·4 g.) had been dissolved was boiled for 30 minutes and the solvent was then evaporated after the addition of water. Benzoylcarbinol was removed by solution in ether and the aqueous liquid was mixed with an excess of dilute sulphuric acid. *3-Keto-2-benzoyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide*, which separated in 66% yield, crystallised from benzene in plates, m. p. 188° (Found: C, 62·6; H, 3·6; S, 11·0. $C_{15}H_{10}O_4S$ requires C, 62·9; H, 3·5; S, 11·2%).

(*b*) 3-Keto-2-benzoyl-2 : 3-dihydrothionaphthen (0·5 g.), suspended in acetic acid (10 c.c.) to which hydrogen peroxide (1 c.c. of 30%) had been added, dissolved after 2 days and the oxidation product, which was identical with the substance obtained as described above, separated.

The substance was recovered unchanged from 10% sodium hydroxide solution after 3 hours' boiling and attempts to obtain an acetyl or benzoyl derivative by the usual methods were unsuccessful. The *diphenylhydrazone*, m. p. 243° after crystallisation from alcohol, was obtained from the substance (1 mol.) and phenylhydrazine (3 mols.) in boiling concentrated benzene solution (Found: N, 12·2. $C_{27}H_{22}O_2N_4S$ requires N, 12·0%).

When the preparation of a monophenylhydrazone of 3-keto-2-benzoyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide was attempted by boiling an alcoholic solution containing phenylhydrazine (1 mol.), 1 : 3-*diphenylthionaphthapyrazole* 5 : 5-*dioxide* (VII, R = Ph) was obtained: this crystallised from acetone in prisms, m. p. 225°, which were insoluble in alkali and responded to Knorr's pyrazole test (*Ber.*, 1893, **26**, 100) (Found: N, 8·2; S, 8·8. $C_{21}H_{14}O_2N_2S$ requires N, 7·8; S, 8·9%).

The *borodiacetate* (VIII) separated in lemon-yellow needles, m. p. 220° (decomp.), when a boiling solution of the substance (II, R = Ph) in acetic anhydride containing boroacetic anhydride was cooled. It was easily decomposed by cold water, yielding the parent substance (II); analysis was made by weighing this product (Found: $C_{15}H_{10}O_4S$, 68·9. $C_{19}H_{15}O_8SB$ requires $C_{15}H_{10}O_4S$, 69·2%). For comparison, the *borodiacetate* of 3-keto-2-benzoyl-2 : 3-dihydrothionaphthen (VIII with S in place of SO_2) was prepared in a similar manner: it formed red prisms which were very slowly decomposed by boiling water (Found: $C_{15}H_{10}O_2S$, 67·1. $C_{19}H_{15}O_6SB$ requires $C_{15}H_{10}O_2S$, 66·7%).

3-*Keto*-2-*phenyl*-2 : 3-*dihydrothionaphthen* 1 : 1-*Dioxide* (II, R = Ph).—(a) Alcohol (50 c.c.) which contained benzyl chloride (6·8 g.) and the potassium salt of *o*-carboxybenzenesulphinic acid (14·2 g.) was boiled for 3 hours. When the potassium chloride had been removed, the sparingly soluble potassium salt (7·8 g.) of *o-carboxyphenylbenzylsulphone* (III, R = Ph) separated. The acid, liberated in the usual manner, crystallised from water in needles, m. p. 126—128° after dehydration at 100° (Found: C, 60·8; H, 4·3; H_2O, 6·2. $C_{14}H_{12}O_4S,H_2O$ requires C, 61·1; H, 4·0; H_2O, 6·1%). The methyl ester (1 mol.), prepared from the silver salt, was heated for 20 minutes with alcohol which contained sodium ethoxide (1 mol.); the solvent was then evaporated, and an aqueous extract of the residue treated with an excess of dilute sulphuric acid. 3-*Keto*-2-*phenyl*-2 : 3-*di*-

hydrothionaphthen 1 : 1-*dioxide*, obtained in 60% yield, crystallised from acetone–alcohol in prisms, m. p. 174° (Found : C, 65·0; H, 3·9. $C_{14}H_{10}O_3S$ requires C, 65·1; H, 3·9%). The yellow alkaline solution yielded unaltered material after 2 hours' boiling.

(b) This phenyl derivative was also obtained by boiling a solution of potassium *o*-carboxybenzenesulphinate (1 mol.) in alcohol which contained benzyl chloride (2 mols.) and treating the resulting solution with sodium ethoxide as usual. When the solvent and other volatile materials had been removed in steam, the remaining aqueous alkaline solution gave the 2-phenyl derivative in 15% yield on treatment with acid. An equal quantity of material which was insoluble in the alkali was identified with the *benzyl* ether (IV) of 3-hydroxy-2-phenylthionaphthen 1 : 1-dioxide synthesised from the 2-phenyl derivative (II, R = Ph) and benzyl chloride in alkaline solution : it separated from acetone–alcohol in prisms, m. p. 146° (Found : C, 72·4; H, 4·6; *M*, 357. $C_{21}H_{16}O_3S$ requires C, 72·4; H, 4·6%; *M*, 348).

3-*Keto*-2-*acetyl*-2 : 3-*dihydrothionaphthen* 1 : 1-*Dioxide* (II, R = $CO{\cdot}CH_3$).—Alcohol (75 c.c.) which contained monochloroacetone (15 g.) and the potassium salt prepared from *o*-carboxybenzenesulphinic acid (15 g.) was boiled for 5 hours. The solution, which contained the sulphone ester (I, R = $CO{\cdot}CH_3$), was treated with sodium ethoxide in the usual manner. Half the volume of solvent was evaporated and the material which separated from the cooled residue was purified from water (charcoal). The required *product* was liberated from the aqueous solution by dilute mineral acid; it separated from benzene–ligroin in prisms, m. p. 164° (Found : C, 53·5; H, 3·7. $C_{10}H_8O_4S$ requires C, 53·6; H, 3·6%). The ketone was recovered unchanged from a boiling alkaline solution. Attempts to prepare the substance by oxidation of 3-keto-2-acetyl-2 : 3-dihydrothionaphthen with hydrogen peroxide were unsuccessful, the chief product being " thioindigo."

The *monophenylhydrazone* was obtained by boiling an alcoholic solution of the ketone with phenylhydrazine (slightly more than 1 mol.) for 3 hours. It crystallised from alcohol in yellow needles, m. p. 210°, which were soluble in aqueous alkali (Found : C, 61·1; H, 4·8; N, 9·2. $C_{16}H_{14}O_3N_2S$ requires C, 61·1; H, 4·8; N, 8·9%). When a solution of the phenylhydrazone in acetic acid containing a few drops of sulphuric acid was warmed at 90° for 1 hour, dehydration was effected and 1-*phenyl*-3-*methylthionaphthapyrazole* 5 : 5-*dioxide* (VII, R = CH_3) was produced. This, isolated from the fluorescent solution by dilution, formed prisms, m. p. 180°, which were insoluble in alkali or acid (Found : N, 9·7. $C_{16}H_{12}O_2N_2S$ requires N, 9·5%). The substance responded to Knorr's pyrazole test.

3-*Keto*-2-o-*nitrophenyl*-2 : 3-*dihydrothionaphthen* 1 : 1-*Dioxide* (II, R = *o*-$NO_2 \cdot C_6H_4$).—The o-*nitrobenzyl* ester (I, R = *o*-$NO_2 \cdot C_6H_4$) of *o*-carboxyphenyl-*o*-nitrobenzylsulphone was prepared from *o*-nitrobenzyl chloride and potassium *o*-carboxybenzenesulphinate in the usual manner; it separated from aqueous acetone in plates, m. p. 156° (Found : C, 55·1; H, 3·7; N, 5·9. $C_{21}H_{16}O_8N_2S$ requires C, 55·3; H, 3·5; N, 6·1%). A solution of this substance (5 g.) in alcohol (100 c.c.) in which sodium (0·25 g.) had been dissolved was boiled ($\frac{1}{2}$ hour); the solvent was then evaporated, and the residue treated with water and ether. The latter solvent removed *o*-nitrobenzyl alcohol. The aqueous solution on treatment with excess of dilute acid yielded 3-*keto*-2-o-*nitrophenyl*-2 : 3-*dihydrothionaphthen dioxide* (2 g.), which crystallised from acetone in prisms, m. p. 187° (Found : C, 55·3; H, 3·2. $C_{14}H_9O_5NS$ requires C, 55·5; H, 3·0%).

Zinc dust was added to a boiling solution of the nitro-compound in acetic acid. The product, separated from the cooled liquid and crystallised from alcohol, gave *thionaphthindole dioxide* (VI) in needles, m. p. 220° (Found : C, 65·6; H, 3·6; S, 12·4. $C_{14}H_9O_2NS$ requires C, 65·9; H, 3·5; S, 12·6%). This substance was also prepared by oxidation of thionaphthindole obtained by McClelland in another manner (J., 1929, 1589).

3-*Keto*-2-p-*aminophenyl*-2 : 3-*dihydrothionaphthen* 1 : 1-*Dioxide* (II, R = *p*-$NH_2 \cdot C_6H_4$).—A concentrated aqueous solution of sodium hydrosulphite was added to a warm (70°) alkaline solution (200 c.c.) of the sodium salt (3 g.) of the 2-*p*-nitrophenyl derivative (J., 1928, 2862) until the red colour of the latter was discharged. When dilute acetic acid was added to the cooled mixture, the required amino-derivative (1·5 g.) was liberated. This separated from alcohol in yellow prisms, m. p. *ca.* 180°, which were too unstable for further purification. It was characterised by the *acetyl* derivative, which formed plates, m. p. 226°, from acetic acid (Found : C, 60·6; H, 4·3. $C_{16}H_{13}O_4NS$ requires C, 60·9; H, 4·1%).

Ethylenedi-o-*carboxyphenylsulphone* (as III, R = CH_2·).—Alcohol (50 c.c.) which contained ethylene dibromide (5 g.) and the potassium salt derived from 10 g. of *o*-carboxybenzenesulphinic acid was boiled (4 hours). The solvent was then evaporated and ethylene dibromide was removed from the residue by a current of steam. The aqueous solution (charcoal) was mixed with excess of sulphuric acid (60%). The *product* liberated (40% yield) crystallised from acetone in needles, m. p. 250° (Found : C, 47·8; H, 3·7. $C_{16}H_{14}O_8S_2$ requires C, 48·2; H, 3·5%). Boiling thionyl chloride converted it into the chloride, from which the *ethyl* ester was obtained in good yield. This formed plates from alcohol and had m. p. 150° (Found :

C, 52·7; H, 5·0; S, 14·2. $C_{20}H_{22}O_8S_2$ requires C, 52·8; H, 4·8; S, 14·1%).

2-Bromo-derivatives.—These substances, except the monobromo-derivative of the parent compound, were obtained by the direct action of the necessary amount of bromine in a suitable solvent, usually acetic acid, and were isolated by dilution with water.

2 : 2-Dibromo-3-keto-2 : 3-dihydrothionaphthen 1 : 1-dioxide (IX with Br in place of H) crystallised from alcohol in needles, m. p. 148°. It liberated iodine from acidified aqueous potassium iodide. Halogen was determined in this manner (*a*) and also by the usual method (*b*) [Found : Br, (*a*) 47·2, (*b*) 47·1. $C_8H_4O_3Br_2S$ requires Br, 47·1%]. The substance dissolved in warm aqueous alkali and the solution was found to contain carboxylic acids, evidently produced by rupture of the thionaphthen ring system.

2-Bromo-3-keto-2 : 3-dihydrothionaphthen 1 : 1-dioxide (IX). A suspension of the 2-carbethoxy-derivative (Feist, *Ber.*, 1925, **58**, 2311) (2 g.) in acetic acid was heated together with a solution of bromine (1·4 g.) in the same solvent for 1½ hours, carbon dioxide being liberated. The *product*, isolated in the usual manner, crystallised from benzene in needles, m. p. 149—150° [Found : C, 36·9; H, 2·0; Br, (*a*) 30·7, (*b*) 30·2. $C_8H_5O_3BrS$ requires C, 36·8; H, 1·9; Br, 30·6%]. It was decomposed by warm aqueous alkali, the ring suffering fission and bromine being eliminated.

2-Bromo-3-keto-2-benzoyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide (IX with COPh in place of H) crystallised from alcohol in needles, m. p. 168° (Found : Br, 22·1. $C_{15}H_9O_4BrS$ requires Br, 21·9%). It dissolved in warm aqueous sodium acetate, and acid liberated the original 2-benzoyl compound from the solution.

2-Bromo-3-keto-2-phenyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide (IX with Ph in place of H) formed plates, m. p. 170°, from which aqueous sodium acetate removed halogen, replacing it by hydrogen (Found : Br, 23·7. $C_{14}H_9O_3BrS$ requires Br, 23·8%).

2-Bromo-3-keto-2-p-nitrophenyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide (as IX) formed plates, m. p. 155°, from acetic acid. The substance behaved in the usual manner with warm sodium acetate solution (Found : Br, 20·8. $C_{14}H_8O_5NBrS$ requires Br, 20·9%). None of these bromine derivatives yielded perbromides or additive compounds with metallic bromides.

The 2-Oxide of 3-Keto-2-phenyl-2 : 3-dihydrothionaphthen 1 : 1-Dioxide (X).—(a) Concentrated hydrochloric acid (3 c.c.) was slowly added to alcohol (25 c.c.) which contained 3-keto-2-phenyl-2 : 3-dihydrothionaphthen dioxide (1 g.) and ethyl nitrite (2·7 c.c. of 15% solution) and the mixture was warmed at 90° for ¼ hour. The *product* (0·8 g.), obtained on cooling, separated from benzene, on

addition of light petroleum, as a microcrystalline powder, m. p. 220° (Found : C, 63·5; H, 3·7; *M*, 515. $C_{28}H_{18}O_7S_2$ requires C, 63·4; H, 3·4%; *M*, 530).

(b) Chromic acid (0·25 g.) was added to acetic acid (15 c.c.) which contained the above phenyl derivative (1·1 g.), and the mixture was warmed and then diluted with water. After purification, the product (1 g.) was identified with that obtained in (a).

When 3-keto-2 : 3-dihydrothionaphthen 1 : 1-dioxide was treated with an excess of nitrous acid under similar conditions to the above, a substance was obtained in almost quantitative yield. It formed plates, which decomposed at 173°, and gave a red solution in cold aqueous alkali; in the warm reagent, decomposition took place, *o*-carboxybenzenesulphinic acid being formed (compare Friedländer, *loc. cit.*) (Found : C, 42·3; N, 9·4; S, 14·0. $C_{16}H_9O_9N_3S_2$ requires C, 42·5; N, 9·3; S, 14·1%). From these data the substance appears to be a *nitroso-oximino* derivative containing the structure >C(NO)·N(OH)·C(NO)< formed by complete replacement of the 2-hydrogen atoms in the parent substance (II, R = H).

3-Keto-2-benzoyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide was not attacked by nitrous acid.

3-*Keto*-2-p-*quino*-2 : 3-*dihydrothionaphthen* 1 : 1-*Dioxide Hydroxide* (XIII, X = OH).—A solution of sodium nitrite (1 g. in 10 c.c.) was slowly added to a cold solution of 3-keto-2-*p*-aminophenyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide (4 g.) in concentrated hydrochloric acid (10 c.c.). The crystalline material which separated was washed with aqueous sodium acetate, with water, and with ether. It formed deep red plates, which decomposed at 123° (Found : C, 58·1; H, 3·3; H_2O, 6·1. $C_{14}H_8O_4S,H_2O$ requires C, 57·9; H, 3·4; H_2O, 6·2%). The substance dissolved in warm concentrated hydrochloric acid, and when chloroplatinic acid was added to the solution the *chloroplatinate* was precipitated in the crystalline state [Found : Pt, 19·9. $(C_{14}H_8O_4S,HCl)_2PtCl_4$ requires Pt, 20·4%]. The *ferrichloride* was obtained in orange crystals by a similar method (Found : Fe, 12·6. $C_{14}H_8O_4S,HCl,FeCl_3$ requires Fe, 11·9%). Both salts were unstable in presence of moisture and decomposed when heated. When a solution of the chloride was diluted, the hydroxide was produced.

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