239. *The Comparative Reactivity of the Carbonyl Groups in the Thionaphthenquinones. Part IV. The Action of Chloramine-T on the Thionaphthenquinones.*

By Charles E. Dalgliesh and Frederick G. Mann.

The nine thionaphthenquinones which have been investigated behave identically when boiled with an excess of chloramine-T in alcohol, furnishing the corresponding disulphonamido-esters of type (VI). Their reaction when similarly treated with one molecular equivalent of chloramine-T divides them, however, into two groups: (*a*) those which furnish solely the disulphide-esters of type (V), and (*b*) those which give the disulphonamido-esters of type (VI), a portion of the thionaphthenquinone being now necessarily unchanged. Evidence is adduced to show by what reactions these products arise from the original thionaphthenquinones.

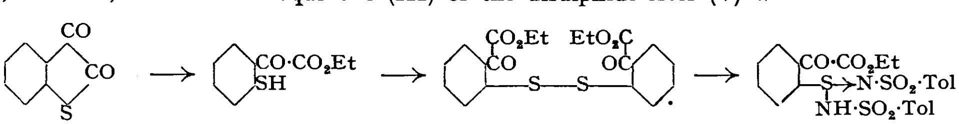
By correlating these results with those obtained in Part II, it is shown that, in general, the thionaphthenquinones which fall in group (*a*) are those which when condensed with thioindoxyls give a high proportion of β-condensations, whereas those which fall in group (*b*) are those which, in these circumstances, give only a very low proportion of β-condensations.

It has been shown by Mann and Pope (J., 1922, **121**, 1052) that many organic sulphides, including some cyclic sulphides, react with chloramine-T (p-$C_6H_4Me{\cdot}SO_2{\cdot}NNaCl,3H_2O$) to give sulphilimines (I; Tol = p-C_6H_4Me–). Clarke, Kenyon, and Phillips (J., 1930, 1225) have shown that thiols, similarly treated, furnish *p*-toluenesulphonimidosulphine-*p*-toluenesulphonylimines (II); the latter compounds are also formed by the action of chloramine-T on disulphides of type R_2S_2 (Alexander and McCombie, J., 1932, 2087). Bulmer and Mann (this vol., p. 670) have further shown that such disulphides are almost certainly the intermediate products in the above conversion of thiols to di-sulphonamido compounds of type (II).

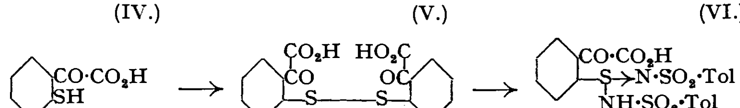
(I.) $R_2S{\rightarrow}N{\cdot}SO_2{\cdot}Tol$ $RS(NH{\cdot}SO_2{\cdot}Tol){\rightarrow}N{\cdot}SO_2{\cdot}Tol$ (II.)

The action of chloramine-T on thionaphthenquinone and various substituted derivatives (cf. Part II, p. 893) has therefore been studied. We find that when an ethyl alcoholic solution of thionaphthenquinone (III) is boiled with one molecular equivalent of chloramine-T, the highly crystalline *diethyl* ester of 2 : 2'-*dicarboxyketodiphenyl disulphide* (V) is formed. This process apparently involved the initial opening of the heterocyclic ring in (III) to give the thiol-ester (IV), which then underwent oxidation by the chloramine-T to the disulphide-ester (V). The identity of this disulphide-ester (V) has been proved (*a*) by molecular weight determinations, (*b*) by repetition of the reaction in methyl and *n*-propyl alcohols whereby the corresponding *dimethyl* and *di-n-propyl* esters were obtained, (*c*) by reduction of disulphides of type (V) to the intermediate thiols (as IV), and (*d*) by hydrolysis of these disulphide-esters of type (V) to the corresponding disulphide-acids (see later).

When, however, either the thioquinone (III) or the disulphide-ester (V) was treated with an excess of



(III.) (IV.) (V.) (VI.)



(VII.) (VIII.) (IX.)

boiling alcoholic chloramine-T, the *ethyl* ester of 2-*carboxyketophenyl*-p-*toluenesulphonimidosulphine*-p-*toluenesulphonylimine* (VI) was formed. The conversion of the disulphide (V) to the compound (VI) is of course an example of Alexander and McCombie's reaction, and it was reasonably certain that the conversion of the thionaphthenquinone (III) into the disulphonamido-compound (VI) proceeded *via* the compounds (IV) and (V) as shown.

A possible although improbable alternative route required investigation. It was possible that the thionaphthenquinone (III) under the influence of the hydrated chloramine-T first underwent hydrolysis to the thiol-carboxylic acid (VII), and that this compound then underwent either esterification to the thiol-ester (IV) or direct oxidation to the disulphide-dicarboxylic acid (VIII). The latter compound, if formed, might then react with an excess of alcoholic chloramine-T, undergoing esterification and disulphonamido formation, with the final production of the compound (VI).

To investigate the possible existence of this alternative route we have, for practical convenience, utilised the 6-ethoxy derivatives instead of the unsubstituted derivatives depicted above. We find that 6-ethoxythionaphthenquinone (as III) is unaffected when refluxed with one molecular equivalent of chloramine-T in aqueous or in 30% aqueous alcoholic solution for 11 hours, but when refluxed with the anhydrous reagent in absolute alcohol readily furnishes the *diethyl* ester of 2 : 2'-*dicarboxyketo*-5 : 5'-*diethoxydiphenyl disulphide* (as V). It is clear therefore that the thiol-carboxylic acid (VII) cannot be an intermediate in these reactions, and that the initial action of the alcoholic chloramine-T on the thioquinone must be direct alcoholysis to the thiol-ester (IV), which then undergoes oxidation to the disulphide-ester (V).

We have also prepared 2 : 2'-*dicarboxyketo*-5 : 5'-*diethoxydiphenyl disulphide* (as VIII) by hydrolysis of the diethyl ester (as V), and also by dissolving the 6-ethoxythionaphthenquinone (as III) in aqueous sodium hydroxide to form the sodium salt of the thiol-carboxylic acid (as VII) and oxidising the latter to the disulphide-acid (as VIII) by the action of sodium tetrathionate (cf. Cambron and Whitby, *Canad. J. Res.*, 1930, **2**, 144; Bulmer and Mann, this vol., p. 675). We find that this disulphide-acid (as VIII), when boiled with chloramine-T in alcoholic solution, is smoothly converted to 2-*carboxyketo*-5-*ethoxyphenyl*-p-*toluenesulphonimidosulphine*-p-*toluenesulphonylimine* (as IX), and that no esterification either to the corresponding disulphide-ester (as V) or to the disulphonamido-ester (as VI) occurred. The existence of this alternative route, involving the intermediate formation of compounds (VII) and (VIII) during the conversion of the thionaphthenquinone (III) to the disulphonamido-ester (VI), is thus disproved.

The reaction of certain substituted thionaphthenquinones with one molecular equivalent of chloramine-T showed one significant difference from that described above. When, *e.g.*, 5-chloro-7-methylthionaphthenquinone (III*c*),* or 4-methylthionaphthenquinone (III*h*), was boiled with one equivalent of chloramine-T in alcoholic solution, only the *disulphonamido* derivative (as VI) resulted, the intermediate disulphide-ester (as V) being absent from the reaction product. In view of the extent of this reaction and the amount of reagent used, the final product necessarily contained unchanged thioquinone. This result must mean that in these cases the conversion of the intermediate disulphide (as V) to the final disulphonamido-ester (as VI) must be a far more rapid process than the initial production of the disulphide from the original thionaphthenquinone.

In certain other cases, *e.g.*, 6 : 7-benzthionaphthenquinone (III*f*), this difference in the relative speeds of the two reactions was however less marked and consequently the action of one equivalent of chloramine-T gave a mixture of the disulphide (V), the disulphonamido-ester (VI) and the unchanged thionaphthenquinone.

It must be emphasised that in no case did the constitution of a substituted thioquinone inhibit the formation of the disulphonamido-ester (as VI), since the latter was always obtained when an excess of alcoholic chloramine-T was employed. The extent to which these compounds were formed when one molecular equivalent of chloramine-T was used must therefore have been determined by the comparative speeds of the reactions involved. Further, the results are not peculiar to chloramine-T, as we have in certain cases duplicated our results using chloramine-B ($Ph\cdot SO_2\cdot NNaCl,3H_2O$).

Not all the twelve thioquinones utilised in Part II have been thus investigated; nevertheless, our results are sufficiently extensive to reveal one interesting feature, namely that this action of chloramine-T is closely connected with the comparative reactivity of the carbonyl groups of the thionaphthenquinone as determined by their behaviour towards the twelve thioindoxyls discussed in Part II. This connection is shown in the table, where the results of the two investigations are correlated. With one exception, those thionaphthen-

Thionaphthen-quinone.	Alcohol used.	Product.	Number of thioindoxyls condensed with quinone (cf. Table I, Part II).	Number of these condensations giving some β-product.
Unsubstituted (III)	EtOH	Disulphide-ester	12	9
	MeOH	,,		
	PrOH	,,		
6-EtO (III*d*)	EtOH	Disulphide-ester	12	12
	MeOH	,,		
5 : 6-Benz (III*g*)	MeOH	Disulphide-ester	12	12
5-Me (III*j*)	EtOH	Disulphide-ester	12	2
6 : 7-Benz (III*f*) *	EtOH	Disulphide-ester + disulphonamido compound	12	3
4 : 5-Benz (III*e*) *	EtOH	Disulphide-ester + disulphonamido compound	12	1
6-Cl-4-Me (III*b*)	EtOH	Disulphonamido compound	12	1
5-Cl-7-Me (III*c*)	EtOH	Disulphonamido compound	12	1
4-Me (III*h*)	EtOH	Disulphonamido compound	11	0

* The mixed product from the thionaphthenquinone (III*e*) contained a higher proportion of disulphonamido compound than that from (III*f*), hence the order of these two quinones in the above table.

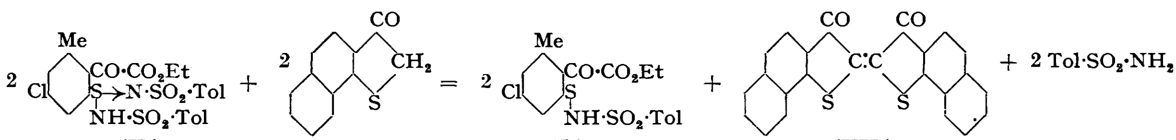
quinones which gave solely disulphide with one equivalent of chloramine-T gave a very high proportion of β-condensations with the thioindoxyls, whereas those which furnished the disulphonamido-compounds gave a

* The letters used to designate the various thionaphthenquinones are those used in Part II (p. 896).

very low proportion of such β-condensations. Only one exception to this generalisation has been detected among the nine thioquinones whose behaviour towards chloramine-T has been studied; 5-methylthionaphthenquinone (III*j*) gave solely the disulphide with chloramine-T, but gave β-condensation with only two of the twelve thioindoxyls.

It is impossible, at present, to give a theoretical explanation of this close correlation of the action of chloramine-T and frequency of β-condensation; it must be dependent on several factors which are unknown or inaccessible. If the initial addition of alcohol to the thionaphthenquinone to form the thiol-ester (IV) is a slow process compared with the subsequent reactions, the thiol-ester would undoubtedly pass right through into the disulphonamido-ester (VI) as fast as it was formed; conversely, if the initial opening of the thioquinone ring is a comparatively rapid process, the subsequent reaction of the thiol-ester would stop at the disulphide-ester stage (V) for lack of chloramine-T. Hence high stability of the thioquinones might be associated with high frequency of β-condensations. Since, however, the comparative speeds of the various reactions are unknown, the particular reaction (or reactions) whose speed in effect determines that of the complete conversion is also unknown; consequently, it is useless to speculate whether the presence of a particular substituent in the quinone affects primarily the speed of conversion (III) → (V), or that of (V) → (VI), or whether it affects both these speeds in different measure.

The properties of the disulphonamido-esters of type (VI) are now being studied. When the 5-*chloro*-3-*methyl disulphonamido-ester* (X) and 6 : 7-benzthioindoxyl in equimolecular quantities were boiled together in alcoholic solution containing a trace of zinc chloride, the former was reduced to the p-*toluenesulphonimido-*



(X.) (XI.) (XII.)

sulphide (XI), whilst the thioindoxyl was oxidised to 6 : 7 : 6′ : 7′-dibenzthioindigo (XII). This reaction is probably general for disulphonamido-esters and thioindoxyls, although at present only this example has been investigated.

Experimental.

The solvent used for recrystallisation, if not ethanol, is named in parenthesis after the compound concerned. Unless otherwise stated, the trihydrated chloramine-T was always employed.

One description of the method of condensation of the thionaphthenquinones with chloramine-T and of the isolation of the products suffices for all. A solution of the two reactants in the appropriate alcohol was refluxed for 6 hours and filtered whilst hot. The insoluble residue was then extracted with boiling alcohol and the latter after filtration was added to the original solution. (The extracted residue in all cases was pure sodium chloride and no indication of an insoluble sodium derivative of a thiol or of a disulphonamido compound was ever obtained.) The alcoholic solution was evaporated to dryness and the residue then recrystallised until pure and identified. The mother-liquors were then again evaporated, and the final residue carefully examined for any product other than *p*-toluenesulphonamide. The 6 hours' refluxing employed in all the following condensations was probably often unnecessarily long, but was deliberately used to ensure that all reaction under these conditions was complete.

Thionaphthenquinone (III).—(1) A mixture of the quinone (2 g.), chloramine-T (3·5 g., 0·95 mol.) and ethanol (80 c.c.) after refluxing gave the *diethyl* ester of 2 : 2′-*dicarboxyketodiphenyl disulphide* (V), pale yellow needles, m. p. 108—109° (Found: C, 57·1; H, 4·5. $C_{20}H_{18}O_6S_2$ requires C, 57·4; H, 4·3%).

(2) Repetition of (1), using methanol (60 c.c.), gave the *dimethyl* ester (as V), yellow plates, m. p. 159—160° (Found: C, 55·4; H, 3·8; S, 16·7. $C_{18}H_{14}O_6S_2$ requires C, 55·4; H, 3·6; S, 16·4%).

(3) Repetition of (1), using *n*-propanol (60 c.c.), gave the *di*-n-*propyl* ester (as V), pale yellow needles, m. p. 101—102° (Found: C, 59·6; H, 5·2. $C_{22}H_{22}O_6S_2$ requires C, 59·2; H, 4·9%).

(4) Repetition of (1), using chloramine-T (13·7 g., 4 mols.) and ethanol (150 c.c.), gave the *ethyl* ester of 2-*carboxyketophenyl*-p-*toluenesulphonimidosulphine*-p-*toluenesulphonylimine* (VI), colourless crystals, m. p. 224° (Found: C, 52·75; H, 4·7; N, 4·9. $C_{24}H_{24}O_7N_2S_3$ requires C, 52·5; H, 4·4; N, 5·1%). Crystallisation from benzene afforded crystals, m. p. 224°, having 0·5 mol. of benzene of crystallisation (Found: C, 55·3; H, 5·0; N, 4·7. $C_{24}H_{24}O_7N_2S_3,\frac{1}{2}C_6H_6$ requires C, 55·5; H, 4·6; N, 4·7%).

6-*Ethoxythionaphthenquinone* (III*d*).—(1) The quinone (3 g.) and chloramine-T (4·2 g., 1·04 mols.) in ethanol (100 c.c.) gave the *diethyl* ester of 2 : 2′-*dicarboxyketo*-5 : 5′-*diethoxydiphenyl disulphide* (as V), pale yellow needles, m. p. 125—126° (Found: C, 56·9; H, 5·1; S, 12·3; *M*, cryoscopic in 0·708% ethylene dibromide solution, 496. $C_{24}H_{26}O_8S_2$ requires C, 56·9; H, 5·1; S, 12·6%; *M*, 506).

(2) Repetition of (1), using anhydrous chloramine-T (3·45 g.) and absolute alcohol (150 c.c.) in specially dried apparatus, gave the same disulphide (2·55 g., 70%), m. p. 125—126° (mixed and unmixed).

(3) Repetition of (1), using either water (480 c.c.) or a mixture of water (210 c.c.) and alcohol (90 c.c.) as solvent, with 11 hours' refluxing, furnished only unchanged thioquinone.

(4) Repetition of (1), using methanol (150 c.c.), gave the *dimethyl* ester of the disulphide (as V), yellow plates, m. p. 184—185° (Found: C, 54·9; H, 4·6; S, 13·7. $C_{22}H_{22}O_8S_2$ requires C, 55·2; H, 4·6; S, 13·4%).

(5) Repetition of (1), using chloramine-T (11·25 g., 2·8 mols.) and ethyl alcohol (150 c.c.), gave the *ethyl* ester of 2-*carboxyketo*-5-*ethoxyphenyl*-p-*toluenesulphonimidosulphine*-p-*toluenesulphonylimine* (as VI), colourless crystals, m. p. 161° (Found: C, 53·1; H, 5·0; N, 4·4. $C_{26}H_{28}O_8N_2S_3$ requires C, 52·7; H, 4·7; N, 4·7%). When this compound was initially obtained by evaporation of the alcoholic mother-liquor, it was necessarily contaminated with toluene-*p*-sulphonamide. The latter, however, was markedly more acidic, and could be readily removed by rapid extraction with cold very dilute aqueous sodium hydroxide; recrystallisation of the washed and dried residue gave the above pure disulphonamido-compound.

A suspension of the powdered 5 : 5′-diethoxy-disulphide ester (as V) in cold alcohol was treated with small fragments of sodium; the liquid became dark red, the disulphide dissolved and, ultimately, the pale yellow sodium derivative of the ethyl ester of 2-carboxyketo-5-ethoxyphenyl thiol (as IV) was precipitated. An alcoholic suspension of this sodium derivative was treated with alcoholic hydrogen chloride, boiled and filtered; the free *thiol* was deposited as colourless needles, m. p. 117—118° (Found : C, 56·4; H, 5·2. $C_{12}H_{14}O_4S$ requires C, 56·7; H, 5·5%).

A suspension of the 5 : 5′-diethoxy-disulphide ester (1 g.; as V) in 10% aqueous sodium hydroxide solution (140 c.c.) was boiled for 15 minutes and the orange solution filtered, cooled, and acidified with hydrochloric acid. The orange precipitate after washing with water and fractional crystallisation from alcohol, furnished first 6-ethoxythionaphthenquinone (0·08 g.), m. p. 162° (mixed and unmixed) and then 2 : *2′-dicarboxyketo-5 : 5′-diethoxydiphenyl disulphide* (as VIII), which separated as a *di-alcoholate*, yellow needles, which on slow heating melted at 184—185° (decomp.) but which underwent partial melting when plunged into a bath at 120° (Found : C, 53·3; H, 5·6; S, 12·2. $C_{20}H_{18}O_8S_2,2C_2H_6O$ requires C, 53·1; H, 5·5; S, 11·8%). This alcoholate, when heated at 80°/0·05 mm. for 7 hours, gave the pure disulphide-*acid* (as VIII), m. p. 184—185° (decomp.) (Found : C, 53·6; H, 4·0. $C_{20}H_{18}O_8S_2$ requires C, 53·3; H, 4·0%). The free acid and its alcoholate readily liberated carbon dioxide from sodium carbonate solution.

The same compound was readily obtained when 6-ethoxythionaphthenquinone (4·5 g.; III*d*) was dissolved in a mixture of N-NaOH (37·5 c.c., 1·05 mol. NaOH) and water (50 c.c.), chilled, and treated with a solution of sodium tetrathionate dihydrate (3·7 g., 1·1 equiv.) in water (100 c.c.). The solution became pale yellow, and after 1 hour was acidified with hydrochloric acid, the above disulphide acid (as VIII) being precipitated; the latter, when crystallised from alcohol, again furnished the yellow needles of the di-alcoholate (4·2 g., 88%), m. p. 188° (Found : C, 53·0; H, 4·8; S, 11·8%).

When this acid was slowly heated to 200° and then maintained at this temperature until effervescence ceased (*ca.* 10 minutes), recrystallisation of the residue from alcohol furnished brown needles, m. p. 158—159°; analysis indicated that loss of carbon monoxide and water had occurred, with the formation of the *anhydride* of 2 : *2′-dicarboxy-5 : 5′-diethoxydiphenyl disulphide* (Found : C, 57·5; H, 4·25. $C_{18}H_{16}O_5S_2$ requires C, 57·45; H, 4·25%). The compound was insoluble in cold aqueous sodium carbonate, but readily dissolved on boiling.

A solution of 2 : 2′-dicarboxyketo-5 : 5′-diethoxy-diphenyl disulphide (2·9 g.; as VIII) and chloramine-T (9 g., 5 mols.) in alcohol (100 c.c.) was refluxed for 5 hours, filtered, evaporated to small bulk and cooled. The semi-solid product was vigorously stirred with aqueous sodium carbonate solution and filtered. The insoluble residue consisted solely of *p*-toluenesulphonamide, but the filtrate, when treated with hydrochloric acid, deposited colourless needles of *2-carboxyketo-5-ethoxyphenyl-*p*-toluenesulphonimidosulphine-*p*-toluenesulphonylimine* (as IX), m. p. 214° (decomp.) from benzene (Found : C, 51·5; H, 4·4; N, 4·7. $C_{24}H_{24}O_8N_2S_3$ requires C, 51·1; H, 4·2; N, 4·9%).

A solution of 6-ethoxythionaphthenquinone (1 g.; III*d*) in warm 5% aqueous sodium hydroxide was cooled and shaken with an excess of dimethyl sulphate. The clear solution was set aside overnight and, on acidification, with hydrochloric acid deposited *methyl* (*2-carboxyketo-5-ethoxyphenyl*) *sulphide*, yellow needles, from aqueous alcohol, m. p. 150° (Found : C, 54·9; H, 4·8. $C_{11}H_{12}O_4S$ requires C, 55·0; H, 5·0%). The compound readily liberated carbon dioxide from cold aqueous sodium carbonate solution, and hence is not the isomeric methyl ester of the free thiol.

5 : *6-Benzthionaphthenquinone* (III*g*).—(1) The quinone (2 g.), chloramine-T (2·5 g., 0·95 mol.) and methanol (60 c.c.) gave the *dimethyl* ester of 3 : *3′-dicarboxyketo-2 : 2′-dinaphthyl disulphide*, yellow plates (benzene), m. p. 192—193° (Found : C, 63·4; H, 3·9. $C_{26}H_{16}O_6S_2$ requires C, 63·7; H, 3·7%).

(2) The quinone (1·2 g.), chloramine-B (5·5 g., 3·75 mols.) and methanol (100 c.c.) furnished the *methyl* ester of *3-carboxyketo-2-naphthyl-benzenesulphonimidosulphine-benzenesulphonylimine*, pale yellow crystals, m. p. 245—246° (Found: C, 54·1; H, 4·0. $C_{25}H_{20}O_7N_2S_3$ requires C, 54·0; H, 3·6%).

5-*Methylthionaphthenquinone* (III*j*).—(1) The quinone (1·6 g.) chloramine-T (2·8 g., 1·1 mols.) and ethyl alcohol (80 c.c.) furnished the *diethyl* ester of 2 : *2′-dicarboxyketo-4 : 4′-dimethyldiphenyl disulphide* (as V), yellow needles, m. p. 155—156° (Found : C, 59·7; H, 5·0; S, 14·7. $C_{22}H_{22}O_6S_2$ requires C, 59·2; H, 4·9; S, 14·4%).

(2) Repetition of (1), using chloramine-T (10·8 g., 4·3 mols.) and ethanol (95 c.c.), gave the *ethyl* ester of the *2-carboxyketo-4-methylphenyl disulphonamido* compound (as VI), colourless crystals, m. p. 200—201° (Found : C, 53·2; H, 5·1. $C_{25}H_{26}O_7N_2S_3$ requires C, 53·4; H, 4·6%).

6 : *7-Benzthionaphthenquinone* (III*f*).—(1) The quinone (1·1 g.), chloramine-T (1·7 g., 1·15 mols.) and ethanol (70 c.c.) furnished a product which after one recrystallisation (alcohol) was a mixture of white and yellow components. The more soluble yellow component was cautiously extracted with a large volume of warm alcohol and the colourless residue, after repeated recrystallisation, gave the *ethyl* ester of the *2-carboxyketo-1-naphthyl disulphonamido* compound (as VI), m. p. 213—214° (Found : C, 56·3; H, 4·2; S, 16·4. $C_{28}H_{26}O_7N_2S_3$ requires C, 56·2; H, 4·4; S, 16·1%). The alcoholic extract, when concentrated and cooled, deposited yellow plates, which after recrystallisation, furnished the *diethyl* ester of 2 : *2′-dicarboxyketo-1 : 1′-dinaphthyl disulphide*, m. p. 162—163° (Found : C, 65·5; H, 4·2; S, 12·2. $C_{28}H_{22}O_6S_2$ requires C, 64·8; H, 4·3; S, 12·4%).

4 : *5-Benzthionaphthenquinone* (III*e*).—(1) The quinone (1·2 g.), chloramine-T (1·8 g., 1·1 mols.) and ethyl alcohol (70 c.c.) gave a crude product which on recrystallisation furnished red needles of the unchanged quinone, m. p. 155—156° (alone and mixed). The mother-liquors, when united and concentrated, gave yellow needles which, after repeated recrystallisation, furnished the *diethyl* ester of 1 : *1′-dicarboxyketo-2 : 2′-dinaphthyl disulphide*, m. p. 103—105° (Found : C, 64·4; H, 4·5; S, 12·2. $C_{28}H_{22}O_6S_2$ requires C, 64·8; H, 4·3; S, 12·4%). The combined filtrates were evaporated to dryness and the residue, repeatedly recrystallised, furnished the disulphonamido compound described below, pale yellow crystals, m. p. 197—198° (alone and mixed).

(2) Repetition of (I), using chloramine-T (7·2 g., 4·5 mols.) and alcohol (75 c.c.), furnished solely the *ethyl* ester of the *1-carboxyketo-2-naphthyl disulphonamido* compound (as VI), m. p. 197—198° (Found : C, 56·4; H, 4·7; S, 15·8. $C_{28}H_{26}O_7N_2S_3$ requires C, 56·2; H, 4·4; S, 16·1%).

6-Chloro-4-methyl-thionaphthenquinone (III*b*).—(1) The quinone (2 g.), chloramine-T (2·3 g., 0·87 mol.) and ethanol (150 c.c.) furnished colourless crystals of the *ethyl* ester of the *5-chloro-2-carboxyketo-3-methylphenyl disulphonamido* compound (X), m. p. 209—210° (Found : C, 50·3; H, 3·4; N, 4·7; S, 16·4. $C_{25}H_{25}O_7N_2ClS_3$ requires C, 50·3; H, 4·2; N, 4·7; S, 16·1%). The use of chloramine-T (3 g., 1·12 mols.) in this experiment gave the same product (1·8 g.). This disulphonamido compound dissolved freely in cold aqueous sodium hydroxide, and was precipitated unchanged on acidification. Solutions of this compound (1·6 g.) and 6 : 7-benzthioindoxyl (0·85 g., 1·6 mols.), each in alcohol (70 and 60 c.c.), were mixed, and refluxed for 8 hours with zinc chloride (0·4 g.), filtered and evaporated to one-third of the original bulk. The mixed product which crystallised was separated by hand into 6 : 7 : 6′ : 7′-dibenzthioindigo (XII) and colourless needles of the *ethyl* ester of *5-chloro-2-carboxyketo-3-methylphenyl* p*-toluenesulphonimido-sulphide* (XI), m. p. 170—171° (Found : C, 50·9; H, 4·3; N, 3·0; Cl, 8·5; S, 13·8. $C_{18}H_{18}O_5NClS_2$ requires C, 50·5; H, 4·2; N, 3·3; Cl, 8·3; S, 14·9%).

(2) Repetition of (1), using chloramine-B (2·6 g., 1·05 mols.) and ethanol (50 c.c.), gave the *ethyl* ester of *5-chloro-2-carboxyketo-3-methylphenyl-benzenesulphonimidosulphine-benzenesulphonylimine*, colourless crystals, m. p. 169—170° (Found : C, 48·9; H, 3·5. $C_{23}H_{21}O_7N_2ClS_3$ requires C, 48·6; H, 3·7%).

5-Chloro-7-methylthionaphthenquinone (III*c*).—(1) The quinone (2 g.), chloramine-T (3 g., 1·12 mols.) and ethanol (90 c.c.) gave the *ethyl* ester of the *4-chloro-2-carboxyketo-6-methylphenyl disulphonamido* compound (as VI), colourless crystals, m. p. 169—170° (Found: C, 50·6; H, 4·2; N, 4·8; S, 16·5. $C_{25}H_{25}O_7N_2ClS_3$ requires C, 50·3; H, 4·2; N, 4·7; S, 16·1%).

4-*Methylthionaphthenquinone* (III*h*).—The quinone (0·8 g.), chloramine-T (1·4 g., 1·1 mols.) and ethanol (60 c.c.) furnished the *ethyl* ester of the 2-*carboxyketo*-3-*methylphenyl disulphonamido* compound (as VI), colourless crytals, m. p. 210—211° (Found: C, 53·5; H, 4·8; N, 4·8; S, 17·6. $C_{25}H_{26}O_7N_2S_3$ requires C, 53·4; H, 4·6; N, 5·0; S, 17·1%).

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