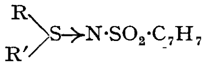
98. *Azoxysulphones, their Preparation and Properties, with Observations on the Structure of Diazotates.*

By W. V. Farrar and J. Masson Gulland.

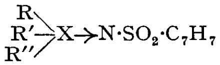
Chloramine-T and related compounds have been shown to condense with a number of aromatic nitroso-compounds to give products which it is proposed to call azoxysulphones. The preparation and properties of some typical members of this new series are described, and the implications of their hydrolysis to diazo-compounds are discussed.

Chloramine-T (sodio-*p*-toluenesulphonchloroamide) reacts readily with thio-ethers, eliminating sodium chloride to give crystalline compounds known as " sulphilimines " (I) (Mann and Pope, J., 1922, 1052); these are clearly similar in structure to sulphoxides, and, when R and R′ are different, can be resolved into optical isomers (Clarke, Kenyon, and Phillips, J., 1927, 188; Holloway, Kenyon, and Phillips, J., 1928, 3000). Reaction of chloramine-T with thiols and with disulphides gives more complex compounds of sulphilimine type (Phillips and Kenyon, J., 1930, 1225; Alexander and McCombie, J., 1932, 2087).

(I.)



$RR'S\rightarrow N\cdot SO_2\cdot C_7H_7$



$RR'R''X\rightarrow N\cdot SO_2\cdot C_7H_7$

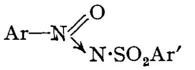
(II.)

Analogously, the condensation of chloramine-T with tertiary phosphines (Mann and Chaplin, J., 1937, 527) and arsines (Mann and Pope, *loc. cit.*; Mann, J., 1932, 958) leads to " phosphinimines " (II, X = P) and " arsinimines " (II, X = As), related to phosphine oxides and arsenoxides in the same way as sulphilimines to sulphoxides.

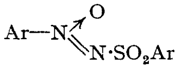
From the above examples, it would seem that, given a compound A capable of being oxidised to A→O, the reaction of A with chloramine-T might lead to $A\rightarrow N\cdot SO_2\cdot C_7H_7$, the group $C_7H_7\cdot SO_2\cdot N$ functioning as a kind of " pseudo-oxygen." This was shown to be incorrect, however, by Mann and Pope (*loc. cit.*), who found that no reaction occurs between dimethylaniline and chloramine-T to give a compound analogous to an amine oxide (II, X = N).

The possibility that chloramine-T would react with nitroso-compounds to give substances of the type (III) appears, however, to have been overlooked. We have investigated this point, and find that reaction does in fact occur, giving the expected products, for which we propose the name " azoxysulphones " by analogy with the " diazosulphones " first prepared by Koenigs (*Ber.*, 1877, **10**, 1531). Thus the product from nitrosobenzene and chloramine-T (III; Ar = Ph, Ar′ = p-C_6H_4Me) is to be called " *phenyl* p-*tolyl azoxysulphone*," the radical attached to nitrogen being named first.

(III.)



$Ar{-}N(\!=\!O)\rightarrow N\cdot SO_2Ar'$



$Ar{-}N(\rightarrow O)\!=\!N\cdot SO_2Ar$

(III*a*.)

It should be noted that two formulæ (III and III*a*) can be written, differing only in electron distribution; the azoxysulphones, therefore, must be regarded as resonance hybrids between these two unperturbed states, and it seems not improbable that the relative stability of these compounds may be due to this feature, whereas compounds of type (II, X = N), lacking resonance, are too labile to exist.

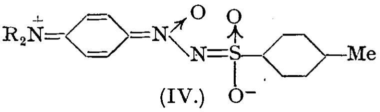
The reaction between nitroso-compounds and chloramine-T proceeds smoothly in pyridine solution at room temperature or on the water-bath. Exclusion of water is not necessary; in fact a 30—40% yield of azoxysulphone is obtained (though mixed with much troublesome tar) when chloramine-T and *p*-nitrosodimethylaniline are simply shaken overnight in aqueous suspension.

Successful condensations were carried out with chloramine-T and the following nitroso-compounds: *p*-nitrosodimethyl- and -diethyl-anilines, nitrosobenzene, *o*- and *p*-nitrosotoluenes, *m*-nitronitrosobenzene, and *p*-nitrosophenetole. *m*-Dinitrosobenzene (Alway and Gortner, *Ber.*, 1905, **38**, 1899) reacted with two molecules of chloramine-T to give a *bisazoxysulphone*. In addition, sodiobenzenesulphonchloroamide (chloramine-B) was condensed with *p*-nitrosodimethylaniline, and reaction of chloramine-B with nitrosobenzene gave the parent compound of the series, *diphenyl azoxysulphone* (III; Ar = Ar′ = Ph).

Some interesting failures of this synthesis were encountered. *p*-Nitrosophenol reacted violently with chloramine-T in pyridine solution, giving brown tarry materials. 5-Nitroso-2-cresol behaved in the same way; in dilute alcoholic solution the reaction was not so vigorous, but the products were similar. *p*-Nitrosoaniline (Fischer and Hepp, *Ber.*, 1887, **20**, 2471) and *p*-nitrosomethylaniline appeared to react normally with chloramine-T in pyridine, but the products were deeply-coloured, amorphous materials only slightly soluble in organic solvents, giving faintly red solutions; they could not be satisfactorily purified, and as they had no basic properties it seems likely that their constitution is more complex than that of the simple azoxysulphone (III, Ar = p-$NH_2\cdot C_6H_4$ or p-$NHMe\cdot C_6H_4$; Ar′ = p-C_6H_4Me). This anomalous behaviour is probably to be connected with the fact that all four of these nitroso-compounds can become quinonoid derivatives by prototropic change. In this connection it is noteworthy that *p*-benzoquinone itself reacts readily with chloramine-T when their solutions in cold alcohol are mixed, giving ill-defined, brownish-purple substances which we have not investigated.

No combination appears to occur between chloramine-T and either *N*-nitroso-compounds, typified by phenylmethylnitrosoamine, or azobenzene under the conditions which suffice for *C*-nitroso-compounds. Our experiments on these points have, however, not been exhaustive.

The azoxysulphones so far prepared by us fall into two well-defined groups. Those not containing a dialkylamino-substituent (such as diphenyl azoxysulphone) are very pale yellow, well-crystallised substances, insoluble in water, but fairly readily soluble in organic solvents; they melt (with one exception) in the region 106—128° without decomposition. The only bisazoxysulphone yet prepared is also pale yellow, though less soluble, and melts at 208° with decomposition. The *p*-dialkylamino-derivatives, on the other hand, are very deeply coloured (red, red-brown, or bronze) and sparingly soluble in low-boiling organic solvents; they all melt around 180° with decomposition. These properties indicate a certain polarity in their structure, which may be perhaps represented by resonance of the azoxysulphone form with a quinonoid form such as (IV). This view is supported by the fact that in concentrated acid solution, where hydrolysis is absent, the cation of the salt is colourless, having presumably the structure (III and IIIa, Ar = $\overset{+}{N}HR_2Ph$–).


(IV.)

Compared with the closely-related diazosulphones, the azoxysulphones are stable compounds. Their reactions have mainly been studied by using the readily accessible phenyl *p*-tolyl azoxysulphone.

Reduction of the azoxysulphone with zinc dust and acetic acid in alcoholic solution gives a good yield of the phenylhydrazide of toluene-*p*-sulphonic acid. This is valuable confirmatory evidence of the structure assigned to the compound. The azoxysulphone is attacked only slowly by boiling acid, neutral, or alkaline permanganate, acetone–permanganate solution, or acid potassium dichromate. Cold concentrated nitric acid has no action, and small quantities of the azoxysulphone can be crystallised unchanged from the warm acid. Bromine in chloroform is not decolorised. This resistance to substitution could be predicted on constitutional grounds.

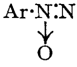
When heated alone, all the monoazoxysulphones decompose with some violence at about 180—200°; sulphur dioxide is evolved and a tarry or coke-like residue is left.

Phenyl *p*-tolyl azoxysulphone is not significantly affected by prolonged boiling with dilute (2N) acids and alkalis. Distillation with 50% sulphuric acid, however, affords considerable quantities of phenol (identified as 2 : 4 : 6-tribromophenol). The resultant reaction can be expressed as: $Ph{\cdot}NO{:}N{\cdot}SO_2{\cdot}C_7H_7 + H_2O \longrightarrow Ph{\cdot}OH + N_2 + C_7H_7{\cdot}SO_3H$, but the formation of phenol strongly suggests that a diazonium salt is an intermediate in the hydrolysis. The following experiments, made to test this theory, show beyond doubt that diazo-compounds are produced when azoxysulphones are hydrolysed by either acids or alkalis, and the theoretical implications are dealt with below. (i) Phenyl *p*-tolyl azoxysulphone dissolves smoothly in ice-cold concentrated sulphuric acid; the solution, when diluted with water, exhibits the reactions of benzenediazonium sulphate solution. Diphenyl azoxysulphone, treated similarly, yielded benzenesulphonic acid. (ii) When the azoxysulphone is refluxed with 30% sodium hydroxide, a solution of benzene *iso*diazotate is formed. (iii) When the azoxysulphone is boiled for a few seconds with aqueous-alcoholic alkali containing β-naphthol, a good yield of benzeneazo-β-naphthol is obtained.

From these experiments it seems a possible assumption that the primary product of the hydrolysis of an azoxysulphone is a *n*-diazotate. This then apparently reacts according to the conditions, giving an azo-compound with β-naphthol, an *iso*diazotate with hot concentrated alkali, a diazonium salt with acid, and a phenol with boiling acid.

There has been much discussion about the constitution of *n*-diazotates, much of which has become meaningless in the light of modern theories of valency. It is clear, however, that only two formulæ are now seriously put forward as possible structures for the *n*-diazotate ion, *viz.*, (V) and (VI). Formula (V) forms the basis of a

(V.) $Ar{\cdot}N{:}N{\cdot}O^-$


$$\underset{\overset{\downarrow}{O}}{Ar{\cdot}N}{:}N^- \qquad \text{(VI.)}$$

modified Hantzsch theory, which regards *n*- and *iso*-diazotates as the *syn*- and *anti*-isomers of the above compound, the correlation between the identity of the isomer and the geometrical configuration being left open. Formula (VI), originally proposed rather speculatively by Bamberger, was later supported (with fresh evidence) by Angeli, who regarded *n*- and *iso*-diazotates as being related in the same way as the two forms of an unsymmetrical azoxy-compound. On this theory, *iso*diazotates are denoted by (V) without reference to geometrical configuration.

The hydrolysis of azoxysulphones to *n*-diazotates and sulphonic acids appears to have a direct bearing on the above question, since a *n*-diazotate of Angeli's structure would be formed if the reaction is regarded as being analogous to the hydrolysis of a sulphonamide : *

$$Ar{\cdot}SO_2{\cdot}NR_2 + H_2O \longrightarrow Ar{\cdot}SO_3H + NHR_2$$
$$Ar{\cdot}SO_2{\cdot}N{:}NO{\cdot}Ar' + H_2O \longrightarrow Ar{\cdot}SO_3H + (Ar'{\cdot}NO{:}N)^- + H^+$$

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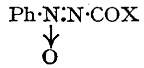
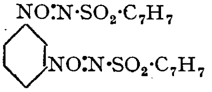
* It has been suggested that azoxysulphones may undergo hydrolysis in the acid solution to aryl*iso*nitroamine $[\underset{\overset{\downarrow}{O}}{Ar{\cdot}N}{:}N{\cdot}O]H$ and a sulphinic acid, and that these may then interact to form a sulphonic acid and $[Ar{\cdot}N{:}N{\cdot}O]H$ or $[\underset{\overset{\downarrow}{O}}{Ar{\cdot}N}{:}N]H$. The investigation of this suggestion is a matter of considerable experimental difficulty, but it should be noted that the existing evidence is against it. First, Bamberger (*Ber.*, 1894, **27**, 1554; 1909, **42**, 1682) showed that

It is not claimed, however, that this constitutes in any sense a proof of Angeli's theory. On the contrary, it is recognised that the hydrolysis of azoxysulphones is a further example of an apparently general reaction. Thus, Angeli (*Gazzetta*, 1917, **47**, I, 215) and Pieroni (*ibid.*, 1922, **52**, II, 32) showed that benzeneazoxycarboxyamide (VII, X = NH_2) is readily hydrolysed (probably *via* the unstable carboxylic acid) by dilute alkali to give a *n*-diazotate, to which Angeli therefore ascribed formula (VI). The question is confused by the assertion of Pieroni and Giannini (*ibid.*, 1924, **54**, I, 162) that the closely-related benzeneazoxycarboxylic ester (VII, X = OEt) gave nitrobenzene and ammonia when hydrolysed by dilute alkali (though hydrolysis in the presence of β-naphthol gave benzeneazo-β-naphthol). These products have never been observed in the decomposition of a *n*-diazotate, so that it is easy to suppose, as did Hantzsch and Strasser (*Ber.*, 1931, **64**, 655), that the intermediate (VI), though showing the coupling reaction, is not a *n*-diazotate. Angeli's amides, however, like our azoxysulphones, do not give nitrobenzene and ammonia on hydrolysis; and a critical examination of Pieroni and Giannini's paper (*loc. cit.*) shows that their evidence is incomplete in many important respects. The azoxy-esters were obtained as yellow oils which were inadequately purified, characterised, and analysed, and the prior presence in them of the nitro-compounds supposed to be obtained on hydrolysis cannot with certainty be excluded; thus the formation of benzeneazoxycarboxylic ester by oxidation of the azo-compound did not proceed smoothly but led also to azoxybenzene and benzoic acid, and Angeli (*Gazzetta*, 1917, **47**, I, 215) observed that nitrobenzene was a by-product of his oxidation of benzeneazocarboxyamide to the azoxy-compound.

(VII.) 

$$\mathrm{Ph\cdot}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{N}}\mathrm{{:}N\cdot COX}$$


(VIII.)

If it is accepted that the products of hydrolysis of all these azoxy-compounds are true *n*-diazotates, either these must be denoted by the Angeli formula (VI), or a transfer of oxygen from one nitrogen atom to the other must be postulated, giving a *n*-diazotate of formula (V). There is neither analogy nor experimental support for this migration, but in any recognition of the Angeli theory recourse must be made to such a transfer in the explanation of, *e.g.*, the facile oxidation of *n*-diazotates to arylnitroamines. On either Hantzsch's or Angeli's theory, therefore, acceptance of oxygen transfer is essential, and since one of the chief drawbacks to the latter hypothesis has always been this very migration, it seems that Angeli's theory merits more serious consideration than it has yet received outside his own circle. It must be admitted, however, that the hydrolysis of azoxysulphones raises, rather than solves, problems, and no pronouncement can yet be made on the structure of the *n*-diazotates.

EXPERIMENTAL.

Diphenyl Azoxysulphone (III, Ar = Ar′ = Ph).—Nitrosobenzene (0·8 g.) and chloramine-B (2·1 g.) were mixed in pyridine (14 c.c.) and left at room temperature overnight; the reaction was completed by heating on the water-bath (80°) for 2 hours. The liquid was then diluted with water (100 c.c.), and the pale brown crystals (1·6 g.; 82%) collected. After two recrystallisations from 95% alcohol, in which it is rather sparingly soluble, *diphenyl azoxysulphone* formed very pale yellow needles, m. p. 123°, readily soluble in acetone and benzene (Found: C, 54·5; H, 4·0; N, 10·8; *M*, modified Rast using *s.*-tribromophenol, 272. $C_{12}H_{10}O_3N_2S$ requires C, 54·9; H, 3·9; N, 10·7%; *M*, 262).

Phenyl p-*Tolyl Azoxysulphone* (III; Ar = Ph, Ar′ = p-MeC_6H_4).—A mixture of nitrosobenzene (1 g.) and chloramine-T (3 g.) in pyridine (10 c.c.) was kept overnight and then heated for 2 hours at 80°. On dilution with water (30 c.c.), an oil separated, which rapidly crystallised. After refrigeration, nearly pure *azoxysulphone* (2·3 g.; 92%) was collected, m. p. 109—111°. Recrystallisation from 95% alcohol gave very pale yellow needles, m. p. 112—113°, very soluble in cold benzene, chloroform, and acetone, moderately in ether and hot alcohol, insoluble in water and light petroleum (Found: C, 56·5; H, 4·9; N, 10·3; S, 11·8; *M*, modified Rast, 254. $C_{13}H_{12}O_3N_2S$ requires C, 56·5; H, 4·4; N, 10·2; S, 11·6%; *M*, 276).

The following substances were made by similar methods, all crystallisations being from 95% alcohol:—

				N, %.		*M*.	
Azoxysulphone.	Description.	M. p.	Yield, %.	Found.	Reqd.	Found.	Reqd.
o-*Tolyl* p-*Tolyl*	Pale yellow prisms	82°	56	9·8	9·7	277	290
Di-p-*tolyl*	Pale yellow plates	106	65	9·8	9·7	300	290
m-*Nitrophenyl* p-*Tolyl*	Very pale yellow needles	122·5—124	87	13·2	13·1	—	—
p-*Phenetyl* p-*Tolyl*	Bright yellow needles	128—128·5	63	8·8	8·8	—	—

p-*Dimethylaminophenyl* p-*Tolyl Azoxysulphone* (III; Ar = p-$NMe_2\cdot C_6H_4$, Ar′ = p-$C_6H'_4Me$).—A mixture of *p*-nitrosodimethylaniline (4·8 g.) and chloramine-T (9·0 g.) was left at room temperature in pyridine (60 c.c.) for 24 hours. It was diluted to *ca.* 350 c.c. with water, and the clear deep-red solution refrigerated overnight, giving a crop of large, dark red needles (8 g., 80%). Subsequent dilution gave a further small, tarry crop. The *azoxysulphone*, recrystallised twice from benzene and once from absolute alcohol, formed reddish-purple prisms, m. p. 182° (decomp.) (Found: C, 56·4; H, 5·4; N, 13·1; S, 10·4. $C_{15}H_{17}O_3N_3S$ requires C, 56·4; H, 5·3; N, 13·1; S, 10·1%). This azoxysulphone can be recrystallised from benzene or glacial acetic acid; it is moderately soluble in cold acetone and hot alcohol, but insoluble in light petroleum. It is a very weak base; boiling 2N-sulphuric acid dissolves it slightly, giving a pink solution, but warm concentrated hydrochloric acid dissolves it easily to a colourless solution, from which the free base is precipitated in crystalline form on dilution.

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phenyl*iso*nitroamine is instantaneously decomposed by mineral acid; in the present instance, therefore, an important competition factor in rates of reaction would come into play. Secondly, Bamberger (*Ber.*, 1898, **31**, 582) showed that alkaline reduction of phenyl*iso*nitroamine yields an *iso*diazotate, whereas it is shown in this communication that dilute alkaline hydrolysis of azoxysulphones gives a *normal* diazotate. In the absence of other evidence, therefore, it would seem to be correct to regard the hydrolysis of azoxysulphones as resulting in the formation of *n*-diazotates and sulphonic acids.

The following substances were made by similar methods, crystallisations being carried out in absolute alcohol:

Azoxysulphone.	Description.	M. p.	Yield, %.	N, %. Found.	N, %. Reqd.	S, %. Found.	S, %. Reqd.
p-*Dimethylaminophenyl Phenyl*......	Bronze needles	175—176°	15*	13·4	13·7	10·7	10·5
p-*Diethylaminophenyl* p-*Tolyl*	Bright red needles	178—179	51	11·9	12·1	9·6	9·2

* Early experiment, not repeated.

m-*Phenylene Bis*-(p-*tolyl Azoxysulphone*) (VIII).—*m*-Dinitrosobenzene (0·2 g.) and chloramine-T (0·85 g.) were heated in pyridine (3 c.c.) at 80° for 4 hours. After dilution with water, the yellow solid was collected and washed with hot alcohol. The *bis-azoxysulphone* separated from glacial acetic acid (50% yield) in curious, lens-shaped, pale yellow crystals, m. p. 208° (decomp.) after darkening above 200°. It is rather sparingly soluble in low-boiling organic solvents (Found: N, 11·5. $C_{20}H_{18}O_6N_4S_2$ requires N, 11·4%).

Reduction of Phenyl p-*Tolyl Azoxysulphone.*—The azoxysulphone (1 g.) was dissolved in boiling alcohol (10 c.c.) containing glacial acetic acid (1 c.c.). Zinc dust was cautiously added, and when the initial violent reaction had subsided the colourless solution was filtered. The filtrate, on dilution with very dilute hydrochloric acid, gave nearly pure *p*-toluenesulphonylphenylhydrazide (0·61 g., 64%), m. p. 154° (decomp.). A mixture with an authentic specimen (m. p. 156°, decomp.) melted at 153—156° (decomp.).

Hydrolyses of Phenyl p-*Tolyl Azoxysulphone.*—(i) The azoxysulphone (0·5 g.) was distilled with 50% sulphuric acid (60 c.c.), soon forming a pale bluish-purple solution. Phenol could be detected in the distillate by its odour, and was converted into 2 : 4 : 6-tribromophenol (51% yield), m. p. 90—92°, mixed m. p. 91—93°.

(ii) The azoxysulphone (0·4 g.) was added in portions to concentrated sulphuric acid (2 c.c.) cooled in an ice-bath, the temperature being kept below 10°. Five minutes after all the crystals had dissolved, the liquid was poured into ice-water (40 c.c.). The clear solution, when poured into excess of an alkaline solution of β-naphthol, gave quantitatively (0·355 g.) nearly pure benzeneazo-β-naphthol, identified by mixed m. p.

(iii) The azoxysulphone (0·5 g.) and β-naphthol (0·25 g.) were dissolved in boiling 95% alcohol (5 c.c.) containing a few drops of 30% sodium hydroxide. A blood-red colour developed; after boiling for 2 mins. the liquid was diluted with water, and the crude azo-compound collected. One recrystallisation from alcohol gave pure benzene azo-β-naphthol, m. p. 130° (0·30 g., or 67%), identified by mixed m. p.

(iv) The azoxysulphone (0·56 g.) was refluxed with 30% sodium hydroxide (15 c.c.) for 30 mins.; frothing then became uncontrollable, and the mixture was cooled, diluted, and filtered. The residue consisted of a red solid (0·26 g.), which was recrystallised from a little alcohol, giving unchanged azoxysulphone (0·16 g., 29%). The red compound present in the alcoholic mother-liquors could not be isolated. The filtrate coupled very slowly with β-naphthol in the cold (pink colour on standing overnight), but when it was acidified, and again made alkaline, coupling was immediate. The *iso*-diazotate was estimated by acidifying and coupling with an alkaline solution of 2-hydroxy-3-naphthoic anilide; the yield of azo-dye was 0·44 g. (59%).

Hydrolysis of Diphenyl Azoxysulphone.—The azoxysulphone (0·3 g.) was dissolved in concentrated sulphuric acid (3 c.c.) at 0°, and after 30 minutes the solution was poured into ice-water, boiled to decompose the diazonium salt, and neutralised with calcium carbonate. The calcium sulphate was collected and washed with water, and the combined filtrate and washings were made faintly acid with hydrochloric acid and freed from sulphate ions with barium chloride. The filtered solution was concentrated to about 10 c.c., mixed with an equal volume of a saturated solution of β-naphthylamine hydrochloride, and cooled to 0°. β-Naphthylamine benzenesulphonate (0·22 g., 64%) (Keyworth, *J. Soc. Chem. Ind.*, 1924, **43**, 341T) separated in colourless plates, m. p. 244° (corr.), of which the identity was confirmed by mixed m. p. with an authentic sample.

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