Preparation and Reactivity of *N*-Phenyl- and *N*-Methyl-*o*-diazoacetylbenzenesulphonamide. A Novel Synthesis of Benzothiazine Dioxides

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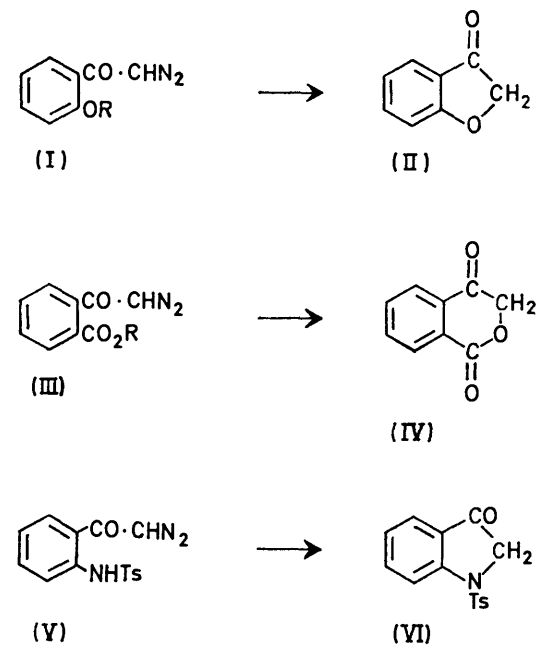
o-Diazoacetylbenzenesulphonyl chloride reacts with aniline and with methylamine to give the corresponding sulphonamides (VIII: R = Ph or Me). With formic acid the diazo-ketones cyclise to give, respectively, 2,3-dihydro-2-phenyl- and -2-methyl-4*H*-1,2-benzothiazin-4-one 1,1-dioxide (X: R = Ph or Me). Toluene-*p*-sulphonic acid effects a similar cyclisation but the thiazine dioxides are in this case accompanied by benzisothiazole derivatives (XIII: R = Ph or Me). Thermolysis of the diazo-ketones also provides the thiazine dioxides along with their 3-oxo-isomers (XIX) arising by cyclisation of the keten which is the product of Wolff rearrangement. Photolysis of *o*-diazoacetyl-*N*-methylbenzenesulphonamide leads only to the Wolff rearrangement product.

THE observation of ready acid-catalysed interaction of a diazoacetyl with an *o*-alkoxy-[1] or *o*-alkoxycarbonyl[2,3] group [(I) ⟶ (II) and (III) ⟶ (IV) respectively] prompted us to investigate the possibility of effecting similar cyclisations on to an *ortho*-substituent containing a nitrogen atom.

Our findings that *N*-(*o*-diazoacetylphenyl)toluene-*p*-sulphonamide (V) undergoes ready acid-catalysed cyclisation to give *N*-*p*-tolylsulphonylindoxyl (VI) were anticipated in publication by Hampel.[4] However, we now report the analogous reactions of *o*-diazoacetyl-*N*-phenylbenzenesulphonamide (VIII; R = Ph) and the corresponding *N*-methyl compound (VIII; R = Me). These were obtained by treating an ethereal solution of *o*-diazoacetylbenzenesulphonyl chloride[5] (VII) with aniline and with methylamine. This appears to be the first recorded example of sulphonamide group formation within a molecule containing a diazoacetyl function. The structure of each of the diazo-ketones was confirmed by elemental analysis, spectral data, and the formation of a triphenylphosphazene. The diazo-ketones dissolved readily in cold dilute sodium hydroxide solution, from which they were precipitated by cautious addition of glacial acetic acid.

When *o*-diazoacetyl-*N*-phenylbenzenesulphonamide (VIII; R = Ph) was treated with formic acid, nitrogen was liberated almost instantaneously and there resulted in high yield a product whose i.r. spectrum showed the presence of a carbonyl group and a sulphonyl group; bands due to NH and diazo-groups were absent. On the basis of these data, and the n.m.r. spectrum, this compound appears to be the thiazinone dioxide (X; R = Ph). This procedure represents a ready synthesis of a ring system which has received little attention apart from the recent work of Zinnes,[6] which is, however, not well adapted to the synthesis of *N*-aryl derivatives such

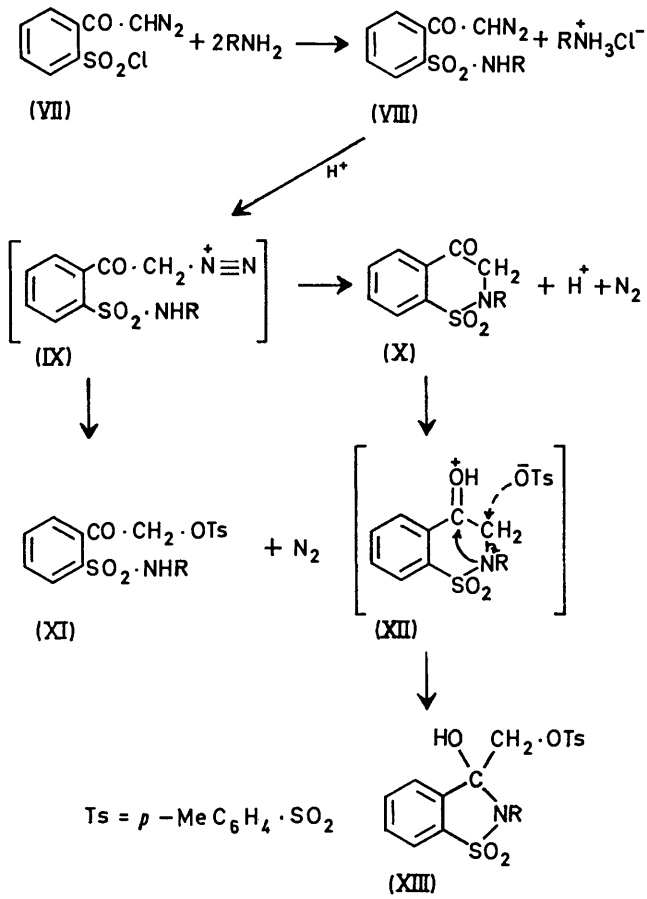


as (X; R = Ph). A similar cyclisation of the *N*-methylsulphonamide (VIII; R = Me) gave, albeit in low yield, a product whose m.p. and spectra accord with

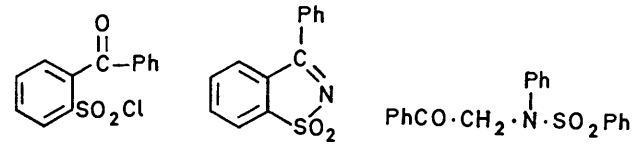
[1] A. Bose and P. Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 4703.
[2] A. Bhati, *J. Org. Chem.*, 1962, **27**, 1183.
[3] P. Duggleby and G. Holt, *J. Chem. Soc.*, 1962, 3579.
[4] W. Hampel, *J. prakt. Chem.*, 1969, **311**, 78.
[5] A. L. Crowther and G. Holt, *J. Chem. Soc.*, 1963, 2926.
[6] H. Zinnes, R. A. Comes, F. R. Zuleski, A. N. Caro, and J. Shavel, jun., *J. Org. Chem.*, 1965, **30**, 2241; H. Zinnes, R. A. Comes, and J. Shavel, jun., *ibid.*, 1966, **31**, 162.

those given by Zinnes [6] for the *N*-methyl derivative (X; R = Me).

Attempts to cyclise either diazo-ketone with a catalytic quantity (0·125 mol. equiv.) of toluene-*p*-sulphonic acid in conditions that gave a high yield of *N*-*p*-tolylsulphonylindoxyl (VI) from the diazo-ketone (V) failed to liberate



all the diazo nitrogen. It proved necessary to add *ca.* 0·4—0·5 mol. equiv. of the sulphonic acid before the reaction was complete. The expected thiazine dioxides were then obtained. The yield of the *N*-methyl derivative (X; R = Me) was higher, and that of the *N*-phenyl derivative (X; R = Ph) lower than when cyclisation was effected with formic acid. In each instance the thiazine dioxide was accompanied by a less soluble compound, which in the case of the *N*-phenyl derivative (VIII; R = Ph) became the major product when the decomposition was effected with 1·6 mol. equiv. of toluene-*p*-sulphonic acid. These compounds gave the analytical figures expected for the acyclic toluene-*p*-sulphonates (XI; R = Me or Ph), the formation of which [(IX) ⟶ (XI)] might be expected to compete with the cyclisation reaction particularly when toluenesulphonate ion is present in excess. However, both carbonyl and >NH bands were absent in the i.r. spectra of these compounds, which, significantly, showed bands attributable to OH groups. Further, the n.m.r. spectrum of the phenyl derivative showed a methylene signal (τ 5·95) as an AB quartet, J_{AB} 10 Hz, suggesting that this group is adjacent to an asymmetric centre. These findings led to the identification of the products as the benzisothiazole derivatives (XIII; R = Me or Ph). Such a product might be expected to arise by interaction of the nitrogen atom and carbonyl group of the acyclic toluene-*p*-sulphonate (XI), similar to that which presumably occurs in the formation of the sultim (XV) obtained when *o*-benzoylbenzenesulphonyl chloride (XIV) is treated with ammonia.[7] Such tertiary alcohols are not unknown: Mustafa and Hilmy [8] have prepared benzisothiazolin-3-ols which carry, at the 3-position, a methyl group rather than the *p*-tolylsulphonyloxymethyl group of (XIII). Unfortunately, these workers give no spectral details.



The observation that the 2-phenylthiazine dioxide (X; R = Ph), the 'normal' product of cyclisation, combines readily with toluene-*p*-sulphonic acid in what is apparently a novel reaction to give the benzisothiazole dioxide (XIII; R = Ph) suggests that such a process occurs in attempted cyclisation reactions and further serves to explain why considerably more than 0·1 mol. equiv. of sulphonic acid is necessary to bring about complete liberation of the diazo nitrogen. It is tempting to suggest that formation of the benzisothiazole derivative (XIII; R = Ph) from toluene-*p*-sulphonic acid and the thiazine dioxide (X) proceeds by attack of the nitrogen atom on the carbon atom of the protonated carbonyl group with synchronous attachment of toluenesulphonate ion to the developing positive charge on the methylene group [(X) ⟶ (XII) ⟶ (XIII)]. However, attempts to bring about an analogous reaction by using sulphuric acid in place of toluene-*p*-sulphonic acid provided a complex mixture, and trifluoroacetic acid did not react with the thiazine dioxide (X). Further, the rearrangement (X) ⟶ (XIII) appears to have special geometrical requirements, since under similar conditions *N*-phenacyl-*N*-phenylbenzenesulphonamide (XVI),[9] the acyclic counterpart of the thiazine dioxide (X), is unaffected by toluene-*p*-sulphonic acid. This suggestion accords with Zinnes' observation that at least one reaction of benzothiazine dioxides has fairly specific structural requirements, and may in part explain our finding that the thiazine dioxide (X; R = Me) does not react with toluene-*p*-sulphonic acid.

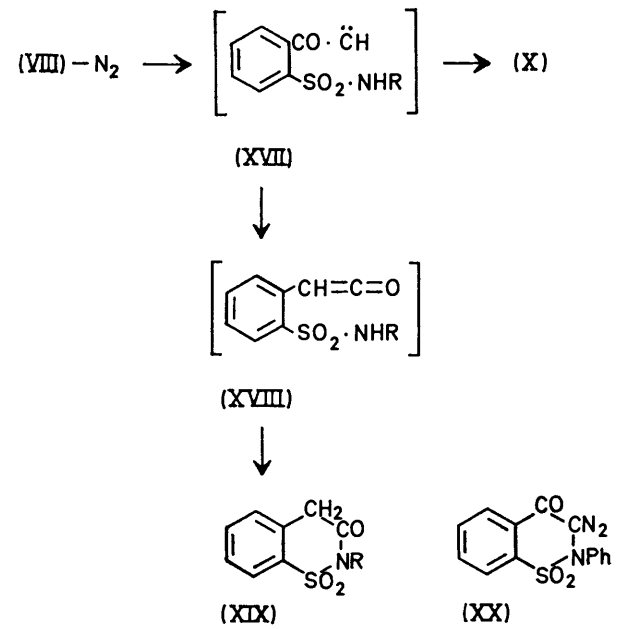
Heating *o*-diazoacetyl-*N*-phenylbenzenesulphonamide

[7] I. Remsen and A. P. Saunders, *Amer. Chem. J.*, 1895, **17**, 354; R. S. Norris, *ibid.*, 1902, **24**, 471.

[8] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1952, 1339.

[9] E. Negishi and A. R. Day, *J. Org. Chem.*, 1965, **30**, 43.

(VIII; R = Ph) in boiling chlorobenzene also provided the thiazine dioxide (X; R = Ph), along with its isomer (XIX; R = Ph). Both of these may be regarded as originating from the acylcarbene (XVII; R = Ph) which may either cyclise directly to the thiazine dioxide (X) or



undergo Wolff rearrangement to the keten (XVIII; R = Ph), cyclisation of which provides the isomeric thiazine dioxide (XIX; R = Ph). The latter process appears to be one of the few recorded examples of a keten reacting with a sulphonamide.

A similar decomposition of the *N*-methylsulphonamide (VIII; R = Me) also yielded a mixture of the two isomeric thiazine dioxides (X and XIX; R = Me). On the other hand photolytic decomposition of this diazoketone provided mainly the product of Wolff rearrangement (XIX; R = Me); its isomer (X; R = Me) was not isolated. When an attempt was made to effect Wolff rearrangement of the *N*-phenylsulphonamide (VIII; R = Ph) with silver benzoate in triethylamine it was necessary to add far more than the normally required catalytic quantity of reagent. Even then the reaction was slow and not all the diazo nitrogen was evolved. The only product isolated from the resulting complex reaction mixture was the unusual diazo-compound (XX).

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 instrument, ^{1}H n.m.r. spectra on Perkin-Elmer R10 and Varian HA100 spectrometers, and mass spectra on an A.E.I. MS902 spectrometer. Gas volumes have been reduced to S.T.P.

N-Phenyl- and N-Methyl-o-diazoacetylbenzenesulphonamide (VIII; R = Ph or Me).—*o*-Chlorosulphonylbenzoyl chloride (11·9 g, 0·052 mol) in ether (50 ml) was added during 30 min to a stirred ice-cold solution of diazomethane (8·40 g, 0·20 mol) in dry ether (1300 ml). When nitrogen evolution was complete (*ca.* 1 h), aniline (9·3 g, 0·10 mol) in ether (50 ml) was added during 30 min. One hour after the addition of aniline was complete the solution was concentrated to low bulk under reduced pressure and filtered to yield a sticky red solid (18·0 g). This material was dissolved in chloroform (500 ml) and extracted repeatedly with water until the washings were neutral. The first extracts (pH 3—5) were colourless; the later ones (pH 5—7) removed the bulk of the red colour from the organic phase. The presence of aniline hydrochloride in the colourless aqueous washings, which gave a strong positive result in a test for chloride ions, was demonstrated by making them strongly alkaline and steam distilling to remove the liberated aniline. The latter was isolated and characterised as benzanilide (3·9 g, 40%), m.p. and mixed m.p. 161—163° (from aqueous ethanol). The chloroform solution was dried ($MgSO_4$) and concentrated to give a brown solid (6·8 g). Trituration of this with methanol (10 ml) gave a yellow product (6·0 g, 38%), m.p. 130—134°, which on recrystallisation from methanol gave o-*diazoacetyl*-N-*phenylbenzenesulphonamide* (VIII; R = Ph) (Found: C, 55·9; H, 3·8; N, 14·2; S, 10·7. $C_{14}H_{11}N_3O_3S$ requires C, 55·8; H, 3·7; N, 13·9; S, 10·6%), m.p. 138—141° (decomp.), $\nu_{max.}$ 3275m (NH), 3110s, 2120s (diazo), 1615s, 1593s, 1484s, 1425s, 1372s (SO_2), 1350s, 1282m, 1225m, 1160s (SO_2), 912s, 902s, 875m, 760s, 749m, 730m, and 700s cm^{-1}, τ ($CDCl_3$) 1·9br (1H, s, disappears on deuteriation, NH), 2·4 (4H, m, *o*-C_6H_4), 2·85 (5H, s, Ph), and 4·3 (1H, s, CO·CHN_2). The diazoketone (0·5 g) and triphenylphosphine (0·56 g) in benzene (10 ml) and ether (50 ml) provided yellow needles of N-(o-*anilinosulphonylphenacylidene*)-PPP-*triphenylphosphadiazene* (0·9 g, 96%) (Found: C, 68·1; H, 4·7; N, 7·5. $C_{32}H_{26}N_3O_3PS$ requires C, 68·2; H, 4·6; N, 7·5%), m.p. 166—167° (decomp.) (from benzene).

When the aniline in the foregoing experiment was replaced by methylamine (3·1 g, 0·1 mol) in ether (140 ml) an analogous, but much cleaner, reaction took place. The crude material, m.p. 105—113°, obtained by evaporation of the ethereal solution to low bulk was freed from methylamine hydrochloride by stirring with water (25 ml) to provide o-*diazoacetyl*-N-*methylbenzenesulphonamide* (VIII; R = Me) (8·7, 72%) (Found: C, 45·5; H, 4·2; N, 17·2; S, 13·3. $C_9H_9N_3O_3S$ requires C, 45·2; H, 4·5; N, 17·5; S, 13·4%), m.p. 113—115° (decomp.) (from ethanol), $\nu_{max.}$ 3240s (NH), 3080s, 2120s (diazo), 1610s, 1370s, 1330s (SO_2), 1165s (SO_2), 875s, 786s, 760s, 755s, and 690s cm^{-1}, τ ($CDCl_3$) 2·0 (m) and 2·5 (m) (4 aromatic H), 4·3br (2H, s, CO·CHN_2 and NH), and 7·4 (3H, d, $J_{Me.NH}$ 6 Hz, Me). When the diazo-ketone in [^{2}H]chloroform was shaken with deuterium oxide the n.m.r. band at τ 4·3 became a sharp singlet (1H) and that at 7·4 τ also became a singlet (3H). With triphenylphosphine as before the diazo-ketone provided N-(o-*methylaminosulphonylphenacylidene*)-PPP-*triphenylphosphadiazene* (Found: C, 64·7; H, 4·9; N, 8·6; S, 6·3. $C_{27}H_{24}N_3O_3PS$ requires C, 64·7; H, 4·8; N, 8·4; S, 6·4%), m.p. 152—153° (decomp.) (from acetonitrile).

Cyclisation Reactions.—(a) *With formic acid.* To o-diazoacetyl-*N*-phenylbenzenesulphonamide (4·0 g, 0·0133 mol) maintained at 21°, 98% formic acid (40 ml) was added all at once. Nitrogen evolution (240 ml; 81%) was complete in 5 min and the formic acid was removed under reduced pressure. Trituration of the sticky residue with ethanol (10 ml) gave a product (2·5 g, 70%), m.p. 95—98°, which on recrystallisation from the same solvent provided

2,3-*dihydro*-2-*phenyl*-4H-1,2-*benzothiazin*-4-*one* 1,1-*dioxide* (X; R = Ph) (Found: C, 61·7; H, 4·1; N, 5·1; S, 11·9. $C_{14}H_{11}NO_3S$ requires C, 61·5; H, 4·0; N, 5·1; S, 11·7%), m.p. 100—101°, $\nu_{max.}$ 2922m, 1712s (C=O), 1590m, 1490s, 1450m, 1444s, 1340s (SO_2), 1325s, 1240s (SO_2), 1132m, 1098w, 1070m, 1050m, 1025w, 1008m, 770s, 759s, 730m, 718m, and 692m cm^{-1}, τ (CCl_4) 2·20 (4H, m, C_6H_4), 3·1 (5H, s, Ph), and 4·93 (2H, s, CH_2), *m/e* 273·0462 (65·4%, $C_{14}H_{11}NO_3S^+$), 209·0834 (1·6%, $C_{14}H_{11}NO^+$), 105·0577 (100·0%, $C_7H_7N^+$), 104·0503 (19·5%, $C_7H_6N^+$), 104·0264 (18·5%, $C_7H_4O^+$), and 91·0413 (41·4%, $C_6H_5N^+$).

When the foregoing procedure was applied to the *N*-methylsulphonamide (VIII; R = Me) (1·9 g, 7·95 mmol) the whole of the diazo nitrogen was rapidly evolved but the crude product was complex. Chromatography on silica gel (30 × 2·5 cm) with toluene–chloroform (4 : 1) as eluant provided 2,3-dihydro-2-methyl-4H-1,2-benzothiazin-4-one 1,1-dioxide (0·2 g, 13%) (Found: C, 51·3; H, 4·3; N, 6·6. Calc. for $C_9H_9NO_3S$: C, 51·2; H, 4·3; N, 6·6%), m.p. 107—109° (from ethanol) (lit.,[6] m.p. 107·5—108·5°), $\nu_{max.}$ 1696s (C=O), 1588m, 1350s (SO_2), and 1175s (SO_2) cm^{-1}, τ ($CDCl_3$) 2·1 (4H, m, aromatic), 5·64 (2H, s, CH_2), and 7·09 (3H, s, Me), *M* 211. The i.r. and n.m.r. data accord with those given by Zinnes.[6] Subsequent elution with solvents of increasing polarity provided several further fractions, all of which were shown by t.l.c. to be complex. With formic acid (3 ml) in acetonitrile (7 ml) the reaction was slower (*ca.* 60 min) and there was no improvement in yield. No reaction took place when an attempt was made to effect the cyclisation with a catalytic quantity of formic acid in acetonitrile.

(b) *With toluene*-p-*sulphonic acid.* To the *N*-phenylsulphonamide (VIII; R = Ph) (2·55 g, 8·5 mmol) in acetonitrile (65 ml) was added toluene-*p*-sulphonic acid (0·19 g, 1·0 mmol) in acetonitrile (10 ml). There was a brisk evolution of nitrogen which subsided after about 30 min and it was necessary to add, during 3·5 h, three further portions of toluenesulphonic acid (1·0 mmol) before the evolution of nitrogen (180 ml, 100%) was complete. The sticky material obtained by removal of the solvent under reduced pressure was agitated with benzene (20 ml) and water (50 ml). The suspended material (A) (1·1 g), m.p. 160—163°, was separated and the residue obtained by removal of the solvent from the dried organic layer was chromatographed on silica gel (35 × 2·5 cm). Elution with 1 : 1 toluene–light petroleum (b.p. 60—80°) gave the 2-phenylthiazine dioxide (X; R = Ph) (1·0 g, 43%). Subsequent elution with toluene–chloroform (4 : 1) gave a further crop of compound (A). The combined products (A), after recrystallisation from acetonitrile provided 2,3-*dihydro*-2-*phenyl*-3-(p-*tolylsulphonyloxymethyl*)-1,2-*benzisothiazol*-3-*ol* 1,1-*dioxide* (XIII; R = Ph) (1·3 g, 36%) (Found: C, 56·9; H, 4·3; N, 2·9; S, 14·7. $C_{21}H_{19}NO_6S_2$ requires C, 56·6; H, 4·3; N, 3·1; S, 14·4%), m.p. 162—164°, $\nu_{max.}$ 3390s (OH), 1595s, 1494m, 1472m, 1454m, 1360s (SO_2), 1300s, 1270m, 1190s, 1175s (SO_2), 1020m, 1012m, 958m, 842s, 838s, 812s, 778s, 740s, and 695m cm^{-1}, τ [$(CD_3)_2SO$] 2·5 (14H, m, aromatic), 5·95 (2H, ABq, J_{AB} 10 Hz, CH_2), and 7·57 (3H, s, Me).

When the diazo-ketone (1·0 g, 3·3 mmol) in acetonitrile (10 ml) was rapidly added to toluene-*p*-sulphonic acid monohydrate (1·0 g, 5·2 mmol) in acetonitrile (10 ml), nitrogen (70 ml, 94%) was rapidly evolved. The solid obtained by removal of the solvent was stirred with water (20 ml) and benzene (30 ml) to give a product which on crystallisation from acetonitrile provided the benzisothiazole dioxide (XIII; R = Ph) (0·73 g, 48%), m.p. and mixed m.p. 161—163°. T.l.c. of the benzene-soluble material indicated the presence of at least five other components.

From a similar reaction of the *N*-methylsulphonamide (VIII; R = Me) (2·1 g, 8·7 mmol) and toluene-*p*-sulphonic acid monohydrate (0·64 g, 3·37 mmol) in acetonitrile (45 ml) there resulted the 2-methylbenzothiazinone dioxide (X; R = Me) (0·35 g, 19%), identical with that already described, and 2,3-*dihydro*-2-*methyl*-3-(p-*tolylsulphonyloxymethyl*)-1,2-*benzisothiazol*-3-*ol* 1,1-*dioxide* (XIII; R = Me) (1·25 g, 39%) (Found: C, 50·4; H, 4·7; N, 3·7; S, 17·1. $C_{16}H_{17}NO_6S_2$ requires C, 50·2; H, 4·4; N, 3·6; S, 16·7%), m.p. 137—139° (from ethanol), $\nu_{max.}$ 3385s,br (OH), 1600m, 1460s, 1400s, 1370s (SO_2), 1360s (SO_2), 1268s, 1192s, 1178s (SO_2), 1165s (SO_2), 1132s, 1099s, 1055s, 1012s, 910s, 842s, 830s, 809s, 793m, 761s, and 668s cm^{-1}, τ ($CDCl_3$) 2·35(m) and 2·7(m) (8H, aromatic), 5·76 (2H, ABq, J_{AB} 11 Hz, CH_2), 6·43br (1H, s, disappearing on deuteriation, OH), 7·34 (3H, s, NMe), and 7·62 (3H, s, CMe). The benzisothiazole derivatives (XIII) apparently exist in more than one form, since the m.p.s of samples slowly fall, although their spectral characteristics remain unchanged. Brief refluxing with the crystallisation solvent restores the m.p. to its original value.

Reaction of Thiazine Dioxides (X) *with Toluene*-p-*sulphonic or Sulphuric Acid.*—The 2-phenylthiazine dioxide (X; R = Ph) (0·45 g, 1·65 mmol) and toluene-*p*-sulphonic acid monohydrate (0·33 g, 1·74 mmol) in acetonitrile (5 ml) were set aside for 12 h. The precipitated material (0·30 g, 41%), m.p. 160—163°, was identical (mixed m.p., i.r. spectra, and t.l.c.) with the foregoing 2-phenylbenzisothiazole dioxide (XIII; R = Ph).

When the toluene-*p*-sulphonic acid in the preceding reaction was replaced by an equivalent quantity of sulphuric acid the thiazine dioxide was decomposed to give, as indicated by t.l.c., a mixture of products, which were not identified.

Wolff Rearrangements of the Diazo-ketones (VIII).—(a) *Thermal.* The diazo-ketone (VIII; R = Ph) (2·2 g, 7·3 mmol) in dry chlorobenzene (100 ml) was added to refluxing chlorobenzene (70 ml) during 30 min. Refluxing was continued until the i.r. spectrum of the material in solution no longer showed a diazo band (*ca.* 10 min). The residue obtained by removal of the solvent under reduced pressure was chromatographed on a silica gel column (40 × 3 cm). Elution with toluene provided the *N*-phenylthiazine dioxide (X; R = Ph) (0·65 g, 33%), m.p. 95—100° (from ethanol), identical (i.r. and n.m.r. spectra) with the material already described. Subsequent elution with toluene–chloroform (5 : 1) gave 2-*phenyl*-2H-1,2-*benzothiazin*-3(4H)-*one* 1,1-*dioxide* (XIX; R = Ph) (0·6 g, 30%) (Found: C, 61·8; H, 4·3; N, 5·3; S, 11·4. $C_{14}H_{11}NO_3S$ requires C, 61·5; H, 4·0; N, 5·1; S, 11·7%), m.p. 117—120° (from ethanol), $\nu_{max.}$ 1725s (C=O), 1600w, 1590w, 1580w, 1485s, 1442m, 1333s (SO_2), 1287s, 1179s (SO_2), 1115s, 1070s, 1022m, 912m, 765s, 725s, 712s, and 700s cm^{-1}, τ ($CDCl_3$) 2·4 (9H, m, aromatic) and 5·75 (2H, s, CH_2), *m/e* 273·0475 (100%, $C_{14}H_{11}NO_3S^+$), 245·0504 (5·7%, $C_{13}H_{11}NO_2S^+$), 209·0842 (2·6%, $C_{14}H_{11}NO^+$), 180·0795 (39·1%, $C_{13}H_{10}N^+$), 154·0074 (3·6%, $C_7H_6O_2S^+$), 137·0046 (12·1%, $C_7H_5SO^+$), 92·0478 (7·3%, $C_6H_6N^+$), and 90·0442 (17·6%, $C_7H_6^+$).

Under similar conditions the methyl analogue (VIII; R = Me) (5·5 g) gave a crude product which was chromatographed on silica gel (42 × 4 cm). Elution with toluene–chloroform (4 : 1) gave, as the only discreet fraction, material

(4·0 g) of m.p. 55—85° which resisted all attempts at separation by recrystallisation or by chromatography. Its n.m.r. spectrum indicated that it was an approximately 1 : 1 mixture of the 2-methylthiazine dioxide (X; R = Me) and its isomer (XIX; R = Me).

(b) *Photolytic.* The diazo-ketone (VIII; R = Me) (2·2 g) in dry benzene (500 ml) was irradiated with a 2W low-pressure u.v. immersion lamp. After 7 days nitrogen evolution (185 ml, 90%) appeared to have ceased and the solvent was removed to give a viscous red oil which was chromatographed on silica gel (45 × 4 cm). Elution with toluene–chloroform (9 : 1) gave a product (0·9 g, 55% based on diazo-ketone consumed) (Found: C, 51·3; H, 4·4; N, 6·5; S, 14·9. $C_9H_9NO_3S$ requires C, 51·2; H, 4·3; N, 6·6; S, 15·2%), m.p. 91·5—92·5° (from ethanol), $\nu_{max.}$ 1710s (CO), 1600w, 1578w, 1478m, 1450m, 1410m, 1335s (SO_2), 1297m, 1288m, 1175s (SO_2), 1125m, 1070m, 1048m, 903s, 865w, 844w, 762s, 736s, and 713m cm^{-1}, τ ($CDCl_3$) 2·27 (4H, m, aromatic), 5·9 (2H, s, CH_2), and 6·72 (3H, s, NMe), *m/e* 211 (44·9%, $C_9H_9NO_3S^+$), 182 (2·3%, $C_8H_9NO_2S^+$), 154 (30·0%, $C_7H_6O_2S^+$), 147 (11·0%, $C_9H_9NO^+$), 137 (33·6%, $C_7H_5OS^+$), 118 (17·8%, $C_8H_7O^+$), and 90 (100·0%, $C_7H_6^+$), identfied as *2-methyl-*2H-1,2-*benzothiazin-*3(4H)-*one* 1,1-*dioxide* (XIX; R = Me). Subsequent elution with toluene–chloroform (1 : 1) yielded unchanged diazo-ketone (0·3 g).

(c) *By silver benzoate and triethylamine.* When this was attempted under the conditions described by Newman and Beal [10] on the *N*-phenyl diazo-ketone (VIII; R = Ph) (3 g, 10 mmol), with 0·1 mol. equiv. of catalyst, 50% of the theoretical volume of diazo nitrogen was evolved during 10 min. Beyond this point nitrogen evolution was very slow despite the addition of further catalyst (0·4 equiv.). After 4 days the originally purple solution had turned red and i.r. spectroscopy showed only a very weak diazo band. Concentration of the solution, after removal of the silver, gave a red oil, chromatography of which on silica gel (50 × 3 cm) proved the mixture to be very complex. The only identifiable material was the most mobile component, eluted with benzene, *3-diazo-2,3-dihydro-2-phenyl-*4H-1,2-*benzothiazin-*4-*one* 1,1-*dioxide* (XX) (0·2 g, 6%) (Found: C, 56·2; H, 3·0; N, 13·9. $C_{14}H_9N_3O_3S$ requires C, 56·3; H, 3·2; N, 14·0%), m.p. 170—173° (decomp.) (from ethanol), $\nu_{max.}$ 2100s (diazo), 1654s, 1480s, 1337s (SO_2), 1302s, 1270s, 1175s (SO_2), 1130s, 960s, 747s, and 690s cm^{-1}, τ ($CDCl_3$) 2·0—3·0 (complex m).

[10] M. S. Newman and P. Beal, *J. Amer. Chem. Soc.*, 1950, **72**, 5163.

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