o-*Mercapto-azo-compounds. Part V.* Preparation and Debenzylation of 2-Benzylthioazobenzene.*

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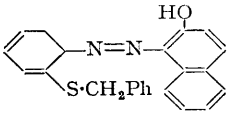
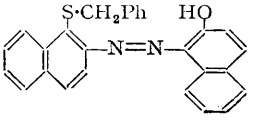
2-Benzylthioazobenzene is converted quantitatively by bromine in glacial acetic acid into azobenzene-2-sulphenyl bromide, which is also obtained, in addition to 3-benzylthiobenzidine dihydrobromide, by the action of hydrobromic acid. The course of the latter reaction is elucidated. Azobenzene-2-sulphenyl bromide is converted by alkali into sodium azobenzene-2-sulphinate and di-(*o*-phenylazophenyl) disulphide. The action of aluminium bromide on 2-benzylthioazobenzene is complex.

As shown in Part IV,* 1-(*o*-benzylthiophenylazo)-2-naphthol (I) and 1-(1-benzylthio-2-naphthylazo)-2-naphthol (II) are rather stable towards hydrobromic acid, but are debenzylated by aluminium bromide in benzene in almost quantitative yield. We have investigated the debenzylation of 2-benzylthioazobenzene (III), the simplest member of this series, which has been obtained by condensing nitrosobenzene with *o*-benzylthioaniline in glacial acetic acid. In contrast to the azonaphthols (I and II), 2-benzylthioazobenzene

(I) 



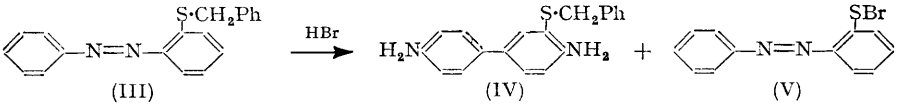
(II)

is debenzylated in a few minutes with hot concentrated hydrobromic acid, alone or, preferably, in mixture with glacial acetic acid. However, as in most of the earlier experiments aiming at the preparation of *o*-mercaptoazo-compounds, this reaction takes an unexpected and complicated course : it yields, instead of 2-mercaptoazobenzene, the sparingly water-soluble dihydrobromide of 3-benzylthiobenzidine (IV) and the water-soluble azobenzene-2-sulphenyl bromide (V).

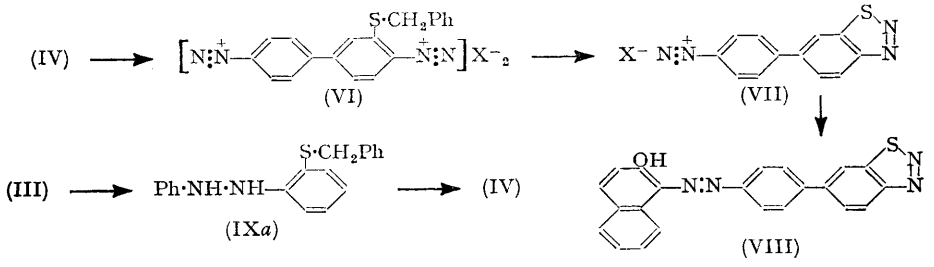
3-Benzylthiobenzidine has been characterised as its dibenzoate and as 6-*p*-(2-hydroxy-1-naphthylazo)phenylbenzo-1-thia-2 : 3-diazole (VIII) obtained by tetrazotisation in

* Part IV, preceding paper.

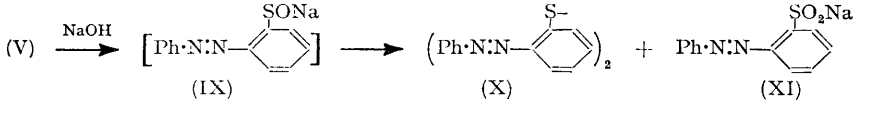
aqueous conditions and coupling with 2-naphthol. The intermediate diazonium salt (VII) is formed by spontaneous debenzylation of the tetrazonium salt (VI), as in the diazotisation of *o*-benzylthioaniline and 1-benzylthio-2-naphthylamine (Part IV). 3-Benzylthiobenzidine



has also been prepared by an unambiguous method. 2-Benzylthioazobenzene (III) is reduced with zinc and sodium hydroxide in ethyl alcoholic solution to 2-benzylthiohydrazobenzene (IX*a*) which when treated with hydrobromic acid undergoes a benzidine rearrangement with formation of the dihydrobromide of (IV).



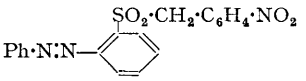
Azobenzene-2-sulphenyl bromide shows many of the characteristic reactions of sulphenyl halides. With dimethylaniline and 2-naphthylamine in glacial acetic acid, it yields *p*-dimethylaminophenyl *o*-phenylazophenyl sulphide and *o*-phenylazophenyl 2-aminonaphthyl sulphide respectively. On addition of sodium hydroxide, its aqueous solution becomes blue-violet, indicating the intermediate formation of sodium azobenzene-2-sulphenate (IX) which slowly disappears to form the orange di-(*o*-phenylazophenyl) disulphide (X) and yellow sodium azobenzene-2-sulphinate (XI) (for the similar behaviour of other sulphenyl halides see, *e.g.*, Zinke and Farr, *Annalen*, 1912, **391**, 51; Fries, *Ber.*, 1912, **45**, 2965; Burawoy and Turner, *J.*, 1950, 469; Kharasch, Potempa, and Wehrmeister, *Chem. Reviews*, 1946, **39**, 269).



Di-(*o*-phenylazophenyl) disulphide (X) is reduced by sodium sulphide or glucose and alkali to the red sodium salt of 2-mercaptoazobenzene which, without isolation, is directly converted by methyl sulphate into 2-methylthioazobenzene, identical with the product obtained from nitrosobenzene with *o*-methylthioaniline in acetic acid. 2-Mercaptoazobenzene itself could not be isolated in a pure state, since it is very easily oxidised to the disulphide, but its existence in solution is shown, not only by the above-mentioned conversion into the methyl ether, but also its extraction by sodium hydroxide from organic solvents. A stable complex salt with copper has also been obtained. Its ease of oxidation is similar to that of its *para*-isomer (cf. Leuckhart, *J. pr. Chem.*, 1890, **41**, 179).

Acidification of the aqueous solution of sodium azobenzene-2-sulphinate yields the free sulphinic acid which, although it crystallises as yellowish prisms from aqueous methyl alcohol, is colourless as a powder and gives colourless solutions in purely organic solvents. The absence of colour appears to exclude the presence of an azo-group in this substance. On the other hand, it shows the characteristic properties of other sulphinic acids. It is unstable to heat and is converted almost quantitatively into azobenzene-2-sulphenyl bromide by boiling hydrobromic–acetic acid, sulphinic acids being known to form the corresponding disulphides or sulphenyl bromides in these conditions (cf. Fries, *loc. cit.*; Fries and Schürmann, *Ber.*, 1914, **47**, 1195). It also forms with 4-nitrobenzyl bromide in

alcoholic sodium hydroxide the crystalline orange-yellow 4-nitrobenzyl *o*-phenylazophenyl sulphone (XII). Whether this sulphinic acid exists as a tautomer of structure (XIII) or (XIV) is under investigation.



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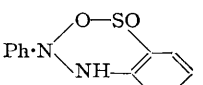
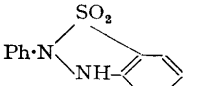
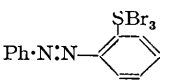


(XIII)



(XIV)



(XV)

The action of hydrobromic acid on 2-benzylthioazobenzene may now be explained. It is initiated by debenzylation of some of the starting material to the thiol, which is quickly dehydrogenated by unchanged 2-benzylthioazobenzene with formation of the disulphide and 2-benzylthiohydrazobenzene. Then, (*a*) the latter undergoes a benzidine rearrangement (as independently confirmed above) to 3-benzylthiobenzidine which is more resistant to debenzylation; and (*b*) the disulphide reacts with hydrobromic acid to form azobenzene-2-sulphenyl bromide and 2-mercaptoazobenzene which again undergoes disproportionation with unchanged starting material. (We have confirmed that in these conditions the disulphide undergoes scission and is converted into the sulphenyl bromide almost quantitatively, the thiol formed being in this case continuously reoxidised by aerial oxidation to the disulphide.) In the total reaction equimolecular quantities of azobenzene-2-sulphenyl bromide and 3-benzylthiobenzidine are formed, in agreement with our findings. The observation that the yield of the sulphenyl bromide obtained in varying conditions consistently approached 50% has been an important factor in the elucidation of the mechanism: it excludes the possibility that 3-benzylthiobenzidine is the product of a side-reaction, unrelated to the debenzylation and formation of the sulphenyl bromide, as in degradation of azobenzene by hydrobromic–acetic acid to a mixture of bromoanilines, 2 : 4-dibromoaniline, and benzidine (Tichwinski, *J. Russ. Phys.-chem. Soc.*, 1903, **35**, 667).

$$2Ph{\cdot}N{:}N{\cdot}C_6H_4{\cdot}S{\cdot}CH_2Ph + 4HBr = Ph{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SBr + H_2N{\cdot}C_6H_4{\cdot}C_6H_3(S{\cdot}CH_2Ph){\cdot}NH_2,2HBr + PhCH_2Br$$

Elucidation of this reaction led to an improved preparation of azobenzene-2-sulphenyl bromide: on addition of an excess of azobenzene to the reaction mixture, the bromide is obtained in almost quantitative yield, azobenzene replacing 2-benzylthioazobenzene as hydrogen acceptor. Addition of one molecule of bromine has the same result; but bromine does not serve as hydrogen acceptor, since even in the absence of hydrobromic acid it rapidly splits 2-benzylthioazobenzene quantitatively into the sulphenyl bromide and benzyl bromide. This provides the most convenient method of debenzylation and in contrast with the slower and more complex action of bromine on 1-(*o*-benzylthiophenylazo)-2-naphthol (I) and 1-(1-benzylthio-2-naphthylazo)-2-naphthol (II) (cf. Part IV). On treatment of 2-benzylthioazobenzene or azobenzene-2-sulphenyl bromide with an excess of bromine in glacial acetic acid, pure azobenzene-2-sulphenyl tribromide (XV) crystallises out. Treatment with sodium hydroxide does not give the blue-violet colour of sodium azobenzene-2-sulphenate as observed with azobenzene-2-sulphenyl bromide (cf. above) and its subsequent disproportionation, but forms a red solution from which sodium azobenzene-2-sulphinate (XI) is obtained in almost quantitative yield, thus supporting structure (XV). Attempts to crystallise this substance led to partial dissociation into the sulphenyl bromide and bromine. It is the first sulphenyl tribromide isolated.

Attempts to debenzylate 2-benzylthioazobenzene with aluminium bromide in benzene proved unsatisfactory, no thiol or disulphide being formed. The reaction was much more complicated than in the case of the azonaphthols (I) and (II). Extraction of the reaction mixture with water and hot hydrobromic acid yielded 35% of azobenzene-2-sulphenyl bromide, together with a high-melting insoluble product which was not investigated.

Experimental

2-*Benzylthioazobenzene* (III).—Nitrosobenzene (5·6 g.), *o*-benzylthioaniline (10 g.), and acetic acid (125 c.c.) were heated at 50° for 15 min. and then set aside overnight. The precipitate of almost pure 2-*benzylthioazobenzene* was filtered off and washed with light petroleum (yield,

12·2 g., 86%). It crystallised from benzene or light petroleum (b. p. 60—80°) as orange needles, m. p. 132—133° (Found: C, 74·4; H, 5·1; N, 9·1. $C_{19}H_{16}N_2S$ requires C, 75·0; H, 5·3; N, 9·2%).

Action of Hydrobromic Acid on 2-Benzylthioazobenzene.—2-Benzylthioazobenzene (3 g.) was refluxed with acetic acid (45 c.c.) and 48% hydrobromic acid (30 c.c.) for 4 min. The orange solution became green and was set aside overnight. The precipitate of *3-benzylthiobenzidine dihydrobromide* (0·85 g., 18·4%) crystallised from ethyl alcohol containing hydrobromic acid as silvery needles, m. p. >300° (Found: C, 48·6; H, 4·3; Br, 34·5. $C_{19}H_{20}N_2SBr_2$ requires C, 48·7; H, 4·3; Br, 34·2%). Water was added to the filtrate, which was extracted with light petroleum to remove benzyl bromide and subsequently with chloroform until the extract did not give the blue-violet colour characteristic for azobenzene-2-sulphenyl bromide with aqueous sodium hydroxide. The chloroform solutions were concentrated to a small volume, and the yellow *azobenzene-2-sulphenyl bromide* (1·4 g., 48%) was precipitated by addition of light petroleum. It crystallised from benzene or ethyl alcohol as yellow needles, m. p. 223—224° (Found: C, 49·4; H, 3·1; H, 9·6. $C_{12}H_9N_2SBr$ requires C, 49·2; H, 3·1; N, 9·6%). The aqueous layer was made alkaline and extracted with ether, from which crude 3-benzylthiobenzidine was obtained (0·55 g., 18·2%). The results were similar, if the reaction time was 2 hr. or the 2-benzylthioazobenzene was refluxed with 48% hydrobromic acid alone, but the dihydrobromide was then less pure.

A solution of the dihydrobromide (2 g.) in hot water (200 c.c.) was cooled and aqueous sodium hydroxide and salt were added. The precipitate of 3-benzylthiobenzidine was crystallised first from aqueous ethyl alcohol (yield, 1 g., 76%) and, finally, from benzene–light petroleum (b. p. 60—80°), forming colourless needles, m. p. 78·5° (Found: C, 74·6; H, 6·0; N, 9·0. $C_{19}H_{18}N_2S$ requires C, 74·5; H, 5·9; N, 9·2%). A suspension of the dihydrobromide (1 g.) in aqueous ethyl alcohol (50 c.c.), 10% aqueous sodium hydroxide (10 c.c.), and benzoyl chloride (4 c.c.) was shaken for 30 min. The precipitated *dibenzoate* (0·75 g., 68%) crystallised from ethyl alcohol as needles, m. p. 203° (sinters at 170—180°; or melts and resolidifies, according to the rate of heating; a molten and resolidified specimen behaved similarly) (Found: C, 76·7; H, 5·2; N, 5·3. $C_{33}H_{26}O_2N_2S$ requires C, 77·0; H, 5·1; N, 5·5%).

6-p-(2-Hydroxy-1-naphthylazo)phenylbenzo-1-thia-2 : 3-diazole (VIII).—Sodium nitrite (0·5 g.) in water (10 c.c.) was added at 0° to a suspension of 3-benzylthiobenzidine dihydrobromide (0·75 g.) in water (200 c.c.) and 48% hydrobromic acid (2 c.c.). A strong smell of benzyl bromide developed. The diazonium solution was added to a solution of 2-naphthol in aqueous sodium hydroxide with stirring. Next morning the red *benzothiadiazole* (0·52 g., 64%) was filtered off. It crystallised from benzene as long red needles, m. p. 227—228°, with a green metallic sheen containing benzene of crystallisation (Found, after drying in a vacuum at 70° for 3 hr.: C, 71·5; H, 4·2; N, 12·9; loss of wt., 8·9. After drying at 100° in a vacuum for 10 hr.: C, 69·0; H, 3·9; N, 14·8. $C_{22}H_{14}ON_4S,\frac{1}{2}C_6H_6$ requires C, 71·3; H, 4·1; N, 13·3; C_6H_6, 9·3. $C_{22}H_{14}ON_4S$ requires C, 69·1; H, 3·6; B, 14·7%).

Alternative Preparation of 3-Benzylthiobenzidine Dihydrobromide.—Zinc dust (12 g.) and 10% aqueous sodium hydroxide (30 c.c.) were added in small amounts alternately with stirring to a boiling solution of 2-benzylthioazobenzene (1·75 g.) in ethyl alcohol (175 c.c.). After 2 hours' refluxing the solution became colourless and was filtered hot, the residue being washed with hot ethyl alcohol (20 c.c.). Hydrobromic acid (48%; 200 c.c.) was added to the combined filtrates. On cooling, the benzidine dihydrobromide separated (2·0 g., 74%). It was converted into the base, the dibenzoate, and the thiadiazole, which were identified by mixed m. p.s.

Action of Hydrobromic Acid on 2-Benzylthioazobenzene in Presence of Azobenzene.—2-Benzylthioazobenzene (3 g.) and azobenzene (3 g.) were refluxed with acetic acid (80 c.c.) and 48% hydrobromic acid (45 c.c.) for 4 min. After cooling and filtration, water was added and the solution extracted with chloroform from which azobenzene-2-sulphenyl bromide (2·7 g. 93%) was obtained by precipitation with light petroleum.

Action of Hydrobromic Acid on 2-Benzylthioazobenzene in Presence of 1 Mol. of Bromine.—Bromine (5·3 g.) in 48% hydrobromic acid (50 c.c.) was added to a solution of 2-benzylthioazobenzene (10 g.) in boiling acetic acid (120 c.c.). The solution was refluxed for 4 min., cooled, and after addition of water extracted with chloroform, from which almost pure azobenzene-2-sulphenyl bromide was isolated as above, having m. p. 212—218° (9·2 g., 95%).

Action of 1 Mol. of Bromine on 2-Benzylthioazobenzene.—Bromine (0·53 g.) in glacial acetic acid (2·5 c.c.) was added to a solution of 2-benzylthioazobenzene (1 g.) in boiling acetic acid (25 c.c.). The solution was refluxed for 4 min.; on cooling, almost pure azobenzene-2-sulphenyl bromide separated in long yellow needles, m. p. 223° (0·75 g., 78·0%). The filtrate was diluted

with water and extracted with chloroform, from which an additional 0·15 g. (15%) of the sulphenyl bromide was obtained.

Action of Sodium Hydroxide on Azobenzene-2-Sulphenyl Bromide.—Aqueous sodium hydroxide (45 c.c.) was added to azobenzene-2-sulphenyl bromide (4 g.) in water (400 c.c.) at 40°. Immediately the solution became blue-violet; orange *di-(o-phenylazophenyl) disulphide* slowly separated (1·85 g., 95%) and was collected after 24 hr. Crystallisation from light petroleum (b. p. 80—100°) gave orange rosettes or needles, m. p. 142° (Found: C, 67·7; H, 4·4; N, 12·9. $C_{24}H_{18}N_4S_2$ requires C, 67·6; H, 4·2; N, 13·1%). After acidification of the filtrate and addition of salt *azobenzene-2-sulphinic acid* slowly separated (0·95 g.). It was dissolved in cold methyl alcohol, an insoluble residue (0·1 g.) being filtered off. Water was added to the alcoholic solution and the solution set aside for a few hours. The pure sulphinic acid crystallised as yellowish prisms, becoming colourless when powdered, m. p. 104°, preceded by a change of colour to orange-red (Found: C, 58·7; H, 4·1; N, 11·5. $C_{12}H_{10}O_2N_2S$ requires C, 58·6; H, 4·1; N, 11·4%). It is unstable to heat and gives colourless solutions with cold ether, chloroform, benzene and alcohol, the latter solution soon becoming yellow.

Copper Complex Salt of 2-Mercaptoazobenzene.—A mixture of finely powdered di-(*o*-phenylazophenyl) disulphide (1 g.), glucose (0·8 g.), 1% aqueous sodium hydroxide (50 c.c.), and ethyl alcohol (100 c.c.) was refluxed for 7 min. The clear red solution obtained after dilution with oxygen-free water (200 c.c.) was quickly cooled and poured into an ice-cold solution of copper sulphate (3 g.) in 1% aqueous sulphuric acid (100 c.c.). After 24 hr., the dark copper complex formed was filtered off, and washed with oxygen-free water, ethyl alcohol and, finally, light petroleum (yield, 0·8 g.; m. p. 228°). It was obtained by precipitation from a chloroform solution with light petroleum as a very dark blue powder, m. p. 228°, insoluble in water, ethyl alcohol, and ether, but sparingly soluble in benzene and chloroform with a blue colour (Found: C, 50·1; H, 3·0; N, 9·0; Cu, 21·9. $C_{12}H_{10}ON_2SCu$ requires C, 49·1; H, 3·4; N, 9·5; Cu, 21·6%).

2-Methylthioazobenzene.—(i) A solution of sodium sulphide nonahydrate (1 g.) and sodium hydroxide (0·5 g.) in water (10 c.c.) and ethyl alcohol (10 c.c.) was added to a suspension of di-(*o*-phenylazophenyl) disulphide (0·3 g.) in boiling ethyl alcohol (30 c.c.). After 4 minutes' refluxing sodium hydroxide (1 g.) in water (100 c.c.) was added, the clear red solution cooled to 40° and methyl sulphate (5 c.c.) added with shaking. The orange *2-methylthioazobenzene* separated slowly (0·3 g., 93%). Crystallisation from methyl alcohol gave orange needles, m. p. 77—78° (Found: C, 68·9; H, 5·6; N, 12·4. $C_{13}H_{12}N_2S$ requires C, 68·4; H, 5·3; N, 12·3%). (ii) Nitrosobenzene (1·5 g.), *o*-methylthioaniline (1·8 g.), and acetic acid (28 c.c.) were kept at 50° for 15 min. and then at room temperature overnight. The precipitated azo-compound (2·1 g., 71%) crystallised from methyl alcohol as orange needles, m. p. and mixed m. p. 77—78°.

Action of Hydrobromic Acid on Di-(o-phenylazophenyl) Disulphide.—Hydrobromic acid (48%; 15 c.c.) was added to a boiling solution of di-(*o*-phenylazophenyl) disulphide (1·0 g.) in acetic acid (25 c.c.). After 3 min. the solution was cooled and set aside overnight. Extraction with chloroform, as described above, yielded almost pure azobenzene-2-sulphenyl bromide (1·2 g., 87%).

Action of Hydrobromic Acid on Azobenzene-2-sulphinic Acid.—Hydrobromic acid (48%; 5 c.c.) was added to a solution of azobenzene-2-sulphinic acid (0·6 g.) in acetic acid (10 c.c.). The mixture was refluxed for a few minutes. Extraction with chloroform yielded almost pure azobenzene-2-sulphenyl bromide, m. p. 220—222° (0·65 g., 91%).

4-Nitrobenzyl o-Phenylazophenyl Sulphone.—Azobenzene-2-sulphinic acid (0·8 g.), 4-nitrobenzyl bromide (0·8 g.), and sodium hydroxide (0·15 g.) in ethyl alcohol (80 c.c.) were refluxed for a few hours. Hot water was added until the solution became turbid. On cooling, *o-phenylazophenyl 4-nitrobenzyl sulphone* separated (1·05 g., 84%), which crystallised from ethyl alcohol as orange plates, m. p. 176° (Found: C, 59·7; H, 4·0; N, 11·3. $C_{19}H_{15}O_4N_3S$ requires C, 59·8; H, 3·9; N, 11·0%).

p-Dimethylaminophenyl p-Phenylazophenyl Sulphide.—Azobenzene-2-sulphenyl bromide (0·6 g.), dimethylaniline (1 c.c.), and acetic acid (10 c.c.) were refluxed for 15 min. Water was added until the solution became turbid. On cooling *p-dimethylaminophenyl p-phenylazophenyl sulphide* separated (0·55 g., 81%). It crystallised from light petroleum (b. p. 60—80°) as orange plates, m. p. 144—145° (Found: C, 72·1; H, 5·7; N, 12·7. $C_{20}H_{19}N_3S$ requires C, 72·1; H, 5·7; N, 12·6%).

2-Aminonaphthyl p-Phenylazophenyl Sulphide.—Azobenzene-2-sulphenyl bromide (0·5 g.), 2-naphthylamine (0·5 g.), and acetic acid (20 c.c.) were refluxed for 10 min. The dark-red solution was added to hot water and, after cooling, the precipitated *2-aminonaphthyl p-phenylazophenyl sulphide* was collected (0·56 g., 92%). It crystallised from light petroleum (b. p.

60—80°) as orange needles, m. p. 124° (Found: C, 73·9; H, 5·0; N, 12·0. $C_{22}H_{17}N_3S$ requires C, 74·4; H, 4·8; N, 11·8%).

Azobenzene-2-sulphenyl Tribromide.—(i) 2-Benzylthioazobenzene (1 g.), bromine (1·16 g., 2·2 mols.), and acetic acid (30 c.c.) were refluxed for 4 min. On cooling, pure *azobenzene-2-sulphenyl tribromide* crystallised almost quantitatively as yellow plates, m. p. 158—160°. Recrystallisation from benzene yielded yellow plates of the same m. p., but there was partial decomposition to the soluble azobenzene-2-sulphenyl bromide (Found: C, 32·5; H, 2·2; Br, 53·1. $C_{12}H_9N_2SBr_3$ requires C, 31·8; H, 2·0; Br, 53·0%).

(ii) Bromine (0·3 g., 1·1 mol.) in acetic acid (1·4 c.c.) was added to a boiling solution of azobenzene-2-sulphenyl bromide (0·5 g.) in boiling acetic acid (10 c.c.). The yellow crystalline tribromide, m. p. 158—160°, separated immediately and was collected after cooling (0·65 g., 84%).

The tribromide (1 g.) dissolved quantitatively in aqueous sodium hydroxide (0·5 g. in 30 c.c.) to a clear red solution. After addition of salt, sodium azobenzene-2-sulphinate (0·55 g., 93%) separated and was collected. It was converted into the free acid, m. p. and mixed m. p. 104° (from dilute methyl alcohol).

Action of Aluminium Bromide on 2-Benzylthioazobenzene.—Freshly distilled aluminium bromide (2·8 g.) in dry benzene (50 c.c.) was shaken with a solution of 2-benzylthioazobenzene (2 g.) in dry benzene (250 c.c.) for 7 days, water was added, and a tarry precipitate filtered off. Both the benzene layer and the precipitated were repeatedly extracted with water, the latter also with hot dilute hydrobromic acid. The combined aqueous solutions were extracted with chloroform, from which azobenzene-2-sulphenyl bromide (0·65 g., 35%) was isolated as described above. The residue, m. p. >300°, was insoluble in all solvents. The benzene layer was concentrated and a small amount of diphenylmethane isolated, having m. p. and mixed m. p. 26° (needles from light petroleum).

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