o-*Mercaptoazo-compounds. Part VII.* Preparation and Debenzylation of 2 : 2′-Dibenzylthioazobenzene.*

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[Reprint Order No. 6410.]

The action of bromine in glacial acetic acid on 2 : 2′-dibenzylthioazobenzene (I), prepared by reduction of 2-benzylthionitrobenzene with lithium aluminium hydride, is investigated. 2-Benzylthioazobenzene-2′-sulphenyl bromide (II), 2-benzylthioazobenzene-2′-sulphenyl tribromide (III), di-[*o*-(*o*′-bromothiophenylazo)phenyl] disulphide (IV), and azobenzene-2 : 2′-di-(sulphenyl bromide) (VI) are isolated and some of their reactions described. The rather unstable 2-benzylthio-2′-mercaptoazobenzene (XV; R = H) and 2 : 2′-dimercaptoazobenzene (XVI; R = H) are formed on reduction of the corresponding disulphide (VII) and polysulphide (XIII) respectively.

THE preparation and debenzylation of 2-benzylthioazobenzene have recently been discussed (Part V *). Treatment with 1 and 2 mols. of bromine yields azobenzene-2-sulphenyl bromide and azobenzene-2-sulphenyl tribromide respectively. The former is converted by zinc into di-(*o*-phenylazophenyl) disulphide and by sodium hydroxide into the same disulphide and sodium azobenzene-2-sulphinate, the latter being also obtained by the action of sodium hydroxide on azobenzene-2-sulphenyl tribromide. 2-Mercaptoazobenzene, formed by reduction of the disulphide with sodium sulphide, could not be obtained analytically pure since it is very readily reoxidised to the disulphide, but its existence was established by conversion with methyl sulphate and alkali into 2-methylthioazobenzene and by the preparation of a stable copper complex salt.

We have now investigated the preparation of 2 : 2′-dibenzylthioazobenzene (I) and its debenzylation by means of bromine. The alkaline reduction of *o*-(benzylthio)nitrobenzene with zinc proved unsatisfactory, whilst the reduction with ammonium chloride and zinc in ethanolic solution yields mainly 2 : 2′-dibenzylthioazoxybenzene and, in addition to some *o*-(benzylthio)aniline, only *ca.* 5% of 2 : 2′-dibenzylthioazobenzene. Nystrom and Brown (*J. Amer. Chem. Soc.*, 1948, **70**, 3738) have shown that lithium aluminium hydride is able to reduce nitro-compounds to the corresponding azo-compounds. Applying this method to *o*-(benzylthio)nitrobenzene, we have obtained in ether a mixture of 2 : 2′-dibenzylthioazoxybenzene and -azobenzene, but in benzene–ether solution only the latter in almost quantitative yield.

The action of bromine on 2 : 2′-dibenzylthioazobenzene (I) yields various products according to the proportion of bromine and the conditions. The stable 2′-benzylthioazobenzene-2-sulphenyl bromide (II) is formed almost quantitatively by the action of one

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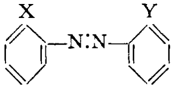
* Parts I, IV, V, and VI, *J.*, 1950, 469; 1954, 82, 90, 4481.

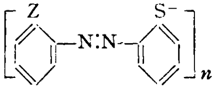
mol. of bromine in boiling acetic acid. It is converted into 2′-benzylthioazobenzene-2-sulphenyl tribromide (III) when shaken with an additional mol. of bromine in cold acetic acid. In boiling solution, the tribromide readily dissociates into the sulphenyl bromide (II) and bromine which, at this higher temperature, attacks the second benzylthio-group with the formation of some di-[*o*-(*o*′-bromothiophenylazo)phenyl] disulphide (IV).

Excess of bromine yields a crystalline product which is probably azobenzene-2 : 2′-di-(sulphenyl tribromide) (V). It is very unstable and, after filtration, quickly loses bromine, leaving as residue the yellow, moderately stable azobenzene-2 : 2′-di(sulphenyl bromide) (VI) which has been characterised by conversion into the corresponding stable water-soluble dichloride and with dimethylaniline into 2 : 2′-di-(*p*-dimethylaminophenylthio)azobenzene (VI; *p*-$S{\cdot}C_6H_4{\cdot}NMe_2$ for SBr). In boiling benzene or acetic acid, the dibromide dissociates into bromine and the stable disulphide (IV), the latter being obtained quantitatively on continuous heating.

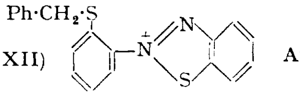
2′-Benzylthioazobenzene-2-sulphenyl bromide (II) reacts with zinc in boiling benzene to yield di-[*o*-(*o*′-benzylthiophenylazo)phenyl] disulphide (VII). On addition of sodium hydroxide to a solution of the sulphenyl bromide (II) in aqueous ethanol a deep blue colour develops immediately owing to formation of sodium 2′-benzylthioazobenzene-2′-sulphenate (VIII). Although the latter could not be isolated, its existence has been established by immediate treatment of the blue solution with methyl sulphate, whereby *o*-(*o*′-benzylthiophenylazo)phenyl methyl sulphoxide (X) is formed. The blue colour disappears after a few hours, disproportionation taking place with formation of the insoluble disulphide (VII) (93%) and the soluble sodium 2′-benzylthioazobenzene-2-sulphinate (IX) which on acidification yields the crystalline orange acid (67%). On longer stirring, the amount of the sulphinic acid increases at the expense of the disulphide. Undoubtedly,the disulphide linkage is slowly attacked by sodium hydroxide, forming the thiol and the sulphenate, the former being readily reoxidised to the disulphide and the latter again undergoing disproportionation with formation of the disulphide and more sulphinic acid.



	X	Y		X	Y
(I)	$S{\cdot}CH_2Ph$	$S{\cdot}CH_2Ph$	(IX)	$S{\cdot}CH_2Ph$	SO_2Na
(II)	$S{\cdot}CH_2Ph$	SBr	(X)	$S{\cdot}CH_2Ph$	SOMe
(III)	$S{\cdot}CH_2Ph$	SBr_3	(XI)	$S{\cdot}CH_2Ph$	$SO_2{\cdot}CH_2Ar$
(V)	SBr_3	SBr_3	(XV)	$S{\cdot}CH_2Ph$	SR
(VI)	SBr	SBr	(XVI)	SR	SR
(VIII)	$S{\cdot}CH_2Ph$	SONa			



	Z	*n*
(IV)	SBr	2
(VII)	$S{\cdot}CH_2Ph$	2
(XIII)	S-	
(XIV)	SONa	2



(XII)

2′-Benzylthioazobenzene-2-sulphinic acid is also obtained almost quantitatively by the action of excess of sodium hydroxide on the tribromide (III). As with the parent azobenzene-2-sulphenyl tribromide (Part V, *loc. cit.*), the blue intermediate colour of the sulphenate is not observed, thus supporting structure (III) for the tribromide. The sulphinic acid (as IX) has been characterised as *o*-(*o*′-benzylthiophenylazo)phenyl nitrobenzyl sulphone (XI) and its structure further confirmed by conversion by hydrobromic acid in acetic acid into the sulphenyl bromide (II), a general reaction of aromatic sulphinic acids (cf. Fries, *Ber.*, 1912, **45**, 2965; Fries and Schürmann, *ibid.*, 1914, **47**, 1195; Parts I and V of this series, *locc. cit.*).

Like azobenzene-2-sulphenyl bromide, its 2′-benzylthio-derivative (II) is converted by double decomposition reactions in aqueous ethanol into the corresponding cyanide, thiocyanate, chloride, iodide, and perchlorate. The iodide is less stable than azobenzene-2-sulphenyl iodide and could not be obtained analytically pure. When heated in solution it readily dissociates into the disulphide and iodine. The properties of these sulphenyl derivatives are similar to those of the parent azobenzene-2-sulphenyl derivatives. As discussed in Part VI (*loc. cit.*), except for the cyanide, they are able to exist as true salts of structure (XII). The quantitative aspect of this problem is being further investigated.

The bisbromothio-disulphide (IV) is converted by zinc in boiling toluene into an orange product which is either the tetrasulphide or the hexasulphide (XIII; $n = 2$ or 3): low solubility precluded a determination of its molecular weight. Addition of aqueous sodium hydroxide to a suspension of the disulphide (IV) in ethanol results in the immediate formation of a blue solution, probably containing the sodium salt (XIV) of the sulphenic acid disulphide. After 20 hours' stirring the blue colour disappears with formation of the insoluble orange polysulphide (XIII) and a red solution yielding on acidification a mixture from which only a colourless substance moderately soluble in ethanol and crystallising as large needles could be obtained in a pure state. Its analysis agrees with the empirical formula $C_{12}H_8O_3N_2S_2$ and the absence of colour excludes the presence of an azo-group. The structure of this product requires further elucidation.

Reduction of the disulphide (VII) and the polysulphide (XIII) with sodium sulphide in ethanol yields 2-benzylthio-2'-mercaptoazobenzene (XV; R = H) and 2 : 2'-dimercapto-azobenzene (XVI; R = H), which like their parent 2-mercaptoazobenzene could not be obtained pure owing to their ease of reoxidation. However, their existence could be established (i) by conversion of the alkaline solutions of the crude isolated products by methyl sulphate or benzyl chloride in good yields into 2-benzylthio-2'-methylthio- (XV; R = Me) and 2 : 2'-dimethylthio-azobenzene (XVI; R = Me) on the one hand, and 2 : 2'-dibenzylthio-azobenzene (XVI; R = CH_2Ph) on the other, and (ii) by the isolation of copper complex salts of the probable structures (XV; R = $\frac{1}{2}$Cu) and (XVI; R = $\frac{1}{2}$Cu) respectively.

EXPERIMENTAL

Reduction of o-*(Benzylthio)nitrobenzene with Zinc and Ammonium Chloride.*—Zinc dust (10 g.) and ammonium chloride (20 g.) in water (80 c.c.) were added alternately with stirring to a boiling solution of *o*-(benzylthio)nitrobenzene (9 g.) in ethanol (350 c.c.). After refluxing for 4 hr., the hot mixture was filtered. On cooling, almost pure 2 : *2'-dibenzylthioazoxybenzene* separated (4·95 g., 61%). Crystallisation from ethanol gave yellow needles, m. p. 155—156° (Found: C, 70·3; H, 5·2; N, 6·0. $C_{26}H_{22}ON_2S_2$ requires C, 70·6; H, 5·0; N, 6·4%). Steam-distillation of the ethanolic filtrate yielded *o*-(benzylthio)aniline (0·3 g., 4%), m. p. 43—44° (after crystallisation from light petroleum), identical with an authentic specimen. The zinc residue was extracted with toluene from which 2 : *2'-dibenzylthioazobenzene* (0·4 g., 5%) was obtained. It is almost insoluble in ethanol and crystallised from toluene as orange needles, m. p. 222—223° (Found: C, 73·4; H, 5·3; N, 6·2. $C_{26}H_{22}N_2S_2$ requires C, 73·2; H, 5·2; N, 6·6%).

Reduction of o-*(Benzylthio)nitrobenzene with Lithium Aluminium Hydride.*—(i) A solution of *o*-(benzylthio)nitrobenzene (10 g.) in dry ether (500 c.c.) was added with stirring to a solution of lithium aluminium hydride (2·75 g.) in dry ether (250 c.c.) at such a rate that the solution was kept gently boiling. After refluxing for 2 hr., the mixture was poured into 10% sulphuric acid (100 c.c.) and ice (500 g.). The precipitate consisting of 2 : 2'-dibenzylthio-azo- and azoxy-benzene was collected. The azoxy-compound (3·5 g., 39%; m. p. 153—154°) was extracted with boiling ethanol, leaving a residue of the slightly impure azo-compound (4·6 g., 53%; m. p. 212—214°). (ii) The experiment was repeated with the exception that *o*-(benzylthio)nitrobenzene (10 g.) in benzene (500 c.c.) was added to the solution of lithium aluminium hydride in ether. Only 2 : 2'-dibenzylthioazobenzene was obtained (8 g., 92%; m. p. 206—210°) which crystallised from toluene as orange needles, m. p. 222—223°, identical with the product obtained in the reduction with zinc and ammonium chloride.

2'-Benzylthioazobenzene-2-sulphenyl Bromide (II).—2 : 2'-Dibenzylthioazobenzene (8 g.), glacial acetic acid (300 c.c.), and bromine (3 g., 1 mol.) were refluxed for 3 min. On cooling, *2'-benzylthioazobenzene-2-sulphenyl bromide* (5·8 g.) slowly crystallised and was collected. Chloroform-extraction of the filtrate yielded a further 1·2 g. (total, 90%). Crystallisation from benzene gave orange-yellow plates, m. p. 183—184° (Found: C, 54·9; H, 4·0; N, 6·8. $C_{19}H_{15}N_2S_2Br$ requires C, 54·9; H, 3·6; N, 6·8%), almost insoluble in ether and light petroleum, sparingly soluble in water, moderately in ethanol and benzene, and easily in chloroform.

2'-Benzylthioazobenzene-2-sulphenyl Tribromide (III).—(i) A suspension of 2 : 2'-dibenzylthio-azobenzene (1 g.) in acetic acid (100 c.c.) was shaken with bromine (0·75 g., 2 mol.) for 3 days.

The orange-yellow, almost pure *sulphenyl tribromide*, m. p. 99—102°, crystallised (1·15 g., 83%) (Found: C, 39·0; H, 2·6; Br, 40·8. $C_{19}H_{15}N_2S_2Br_3$ requires C, 39·7; H, 2·6; Br, 41·7%). No improvement in purity was effected by crystallisation from acetic acid or benzene, which caused partial dissociation into the monobromide and bromine. (ii) A suspension of 2′-benzylthioazobenzene-2-sulphenyl bromide (1 g.) in glacial acetic acid (100 c.c.) was shaken with bromine (0·4 g., 1 mol.) for 3 days. The precipitate of almost pure crystalline tribromide, m. p. 99—102°, was collected (1·3 g., 94%). (iii) A suspension of the tribromide (1 g.) in acetic acid (50 c.c.) was shaken with bromine (0·63 g., 2 mol.) at room temperature for 2 days. No reaction occurred, the starting material being recovered quantitatively.

Di-[o-(o′-*bromothiophenylazo*)*phenyl*] *Disulphide* (IV).—(i) A suspension of 2 : 2′-dibenzylthioazobenzene (2 g.) in acetic acid (60 c.c.) was refluxed with bromine (1·5 g., 2 mol.) for 3 min. On cooling, a tar separated (1·4 g.). The filtrate was extracted with chloroform and the red tar with benzene, from which solvents 2′-benzylthioazobenzene-2-sulphenyl bromide was obtained (1·2 g., 62%). The solid residue consisted of crude *bisbromothio-disulphide*, which crystallised from chlorobenzene or acetic acid as yellow needles, m. p. 264—265° (0·4 g., 24%) (Found: C, 44·7; H, 2·4; N, 8·7. $C_{24}H_{16}N_4S_4Br_2$ requires C, 44·5; H, 2·5; N, 8·6%). (ii) 2′-Benzylthioazobenzene-2-sulphenyl bromide (1 g.), acetic acid (30 c.c.), and bromine (0·4 g., 1 mol.) were refluxed for 3 min. On cooling, a red tar separated. The mixture was worked up as above. Starting material (0·45 g.) was recovered, and the yield of disulphide was 0·3 g. (70%). (iii) The experiment was repeated, but boiling continued for 1 hour, the corresponding yields then being 0·2 g. and 0·5 g. (79%). (iv) 2′-Benzylthioazobenzene-2-sulphenyl bromide (1 g.), acetic acid (30 c.c.), and bromine (0·8 g., 2 mol.) were refluxed for 3 min. No starting material was recovered and the yield of disulphide was 0·6 g. (77%). (v) No reaction occurred when a suspension of the bisbromothio-disulphide (0·5 g.) in acetic acid (50 c.c.) was shaken with bromine (0·124 g., 1 mol.) for 2 days.

Azobenzene-2 : 2′-*di*(*sulphenyl Bromide*) (VI).—(i) A suspension of 2 : 2′-dibenzylthioazobenzene (2 g.) in acetic acid (60 c.c.) was refluxed with bromine (3 g., 4 mol.) for 3 min. On cooling, orange plates, m. p. 134—136°, contaminated with a red tar, separated and were collected. The fuming unstable orange plates, which might be azobenzene-2 : 2′-di(sulphenyl tribromide) (V), quickly lost bromine in air and changed to a more stable yellow product. Rapid crystallisation from acetic acid containing a drop of bromine yielded hydrated *azobenzene*-2 : 2′-*di*(*sulphenyl bromide*), m. p. 199° (Found: C, 33·7; H, 2·3; Br, 38·8. $C_{12}H_8N_2S_2Br_2,H_2O$ requires C, 34·1; H, 2·3; Br, 37·9%), sparingly soluble in water and moderately in ethanol. Crystallisation after prolonged heating either of the original orange plates or of the di(sulphenyl bromide) from chlorobenzene or acetic acid gave pure bisbromothio-disulphide (IV), m. p. 264—265°. (ii) The bisbromothio-disulphide (0·5 g.), acetic acid (50 c.c.), and bromine (0·5 g., 4 mol.) were shaken for 2 days. The filtered red solid changed in air with liberation of bromine into the yellow azobenzene-2 : 2′-di(sulphenyl bromide), m. p. 199° (0·5 g., 80%).

Azobenzene-2 : 2′-*di*(*sulphenyl Chloride*).—To pure azobenzene-2 : 2′-di(sulphenyl bromide) (0·5 g.) suspended in acetic acid (100 c.c.) was added concentrated hydrochloric acid (100 c.c.) and the mixture shaken for 6 hr. The resulting solution was diluted with water and extracted with chloroform, which after drying was evaporated to a small volume. On addition of light petroleum *azobenzene*-2 : 2′-*di*(*sulphenyl chloride*) (0·25 g., 63%) separated. It crystallised from chlorobenzene as a pale yellow solid, m. p. 215°, soluble in water and ethanol (Found: C, 45·4; H, 2·5; N, 8·3. $C_{12}H_8N_2S_2Cl_2$ requires C, 45·7; H, 2·5; N, 8·8%).

2′-*Benzylthioazobenzene*-2-*sulphenyl Chloride*.—A solution of 2′-benzylthioazobenzene-2-sulphenyl bromide (0·5 g.) in warm ethanol (65 c.c.) was added to water (250 c.c.) and concentrated hydrochloric acid (20 c.c.), and the whole extracted with chloroform, from which, after evaporation, the *chloride* was obtained (0·35 g., 78%). It crystallised from benzene as orange-yellow needles, m. p. 160—161° (sintering at 96°), containing benzene of crystallisation which could be removed only *in vacuo* at 100° for 5 hr. (Found, after 3 hours' drying at 70° *in vacuo*: C, 64·4; H, 4·6; N, 7·0. $C_{19}H_{15}N_2S_2Cl,\frac{1}{2}C_6H_6$ requires C, 64·5; H, 4·4; N, 6·9%; after drying to constant weight at 100° *in vacuo*: C, 60·9; H, 3·8; loss, 9·5. $C_{19}H_{15}N_2S_2Cl$ requires C, 61·5; H, 4·1; loss, 9·5%).

2′-*Benzylthioazobenzene*-2-*sulphenyl Iodide*.—A solution of the bromide (0·5 g.) in warm ethanol (65 c.c.) was added to an ice-cold solution of potassium iodide (3 g.) in water (200 c.c.). There was immediate deposition of the orange-brown *iodide*, m. p. 190—191°, which was filtered off, washed, and dried (Found: C, 47·3; H, 2·9. $C_{19}H_{15}N_2S_2I$ requires C, 49·3; H, 3·3%). Crystallisation from benzene or slow crystallisation from ethanol yielded pure di-[*o*-(*o*′-benzylthiophenylazo)phenyl] disulphide (VII), m. p. 230—231°, described below.

2′-Benzylthioazobenzene-2-sulphenyl Perchlorate.—A solution of 2-benzylthioazobenzene-2-sulphenyl bromide (0·5 g.) in warm ethanol (65 c.c.) was added to an ice-cold solution of sodium perchlorate (3 g.) in water (200 c.c.). The precipitate of almost pure *perchlorate* (0·5 g., 86%) was filtered off. It crystallised from aqueous ethanol as orange needles, m. p. 113—115° (with detonation) (Found : C, 52·5; H, 3·3. $C_{19}H_{15}O_4N_2S_2Cl$ requires C, 52·5; H, 3·5%).

2′-Benzylthioazobenzene-2-sulphenyl Thiocyanate.—A solution of the same bromide (0·5 g.) in warm ethanol (70 c.c.) was added to an ice-cold solution of potassium thiocyanate (2 g.) in water (100 c.c.). The slowly formed precipitate of the *thiocyanate* was collected and washed with water (0·35 g., 78%). It crystallised from benzene as yellow-orange needles, m. p. 106° (Found : C, 61·6; H, 3·8; N, 10·4. $C_{20}H_{15}S_3N_3$ requires C, 61·1; H, 3·8; N, 10·6%).

2′-Benzylthioazobenzene-2-sulphenyl Cyanide (*2-Benzylthio-2′-thiocyanatoazobenzene*).—The above experiment was repeated, but with potassium cyanide in place of potassium thiocyanate. The precipitated *cyanide* (0·49 g., 83%) was filtered off and washed with water. It crystallised from ethanol as orange needles, m. p. 129—130° (Found : C, 66·5; H, 4·0; N, 11·8. $C_{20}H_{15}N_3S_2$ requires C, 66·5; H, 4·0; N, 11·6%).

Action of Zinc on 2′-Benzylthioazobenzene-2-sulphenyl Bromide.—This bromide (1 g.), benzene (100 c.c.), and zinc dust (5 g.) were refluxed for 20 min. The hot solution was filtered and concentrated. On cooling, *di-*[o-(o′-*benzylthiophenylazo*)*phenyl*] *disulphide* separated (0·65 g., 81%). Crystallisation from benzene gave a yellow-orange solid, m. p. 230—231° (Found : C, 67·9; H, 4·6; N, 8·1. $C_{38}H_{30}N_4S_3$ requires C, 68·1; H, 4·5; N, 8·4%).

Action of Sodium Hydroxide on 2′-Benzylthioazobenzene-2-sulphenyl Bromide.—(i) 10% Sodium hydroxide solution (20 c.c.) was added with stirring to a suspension of the bromide (2 g.) in water (100 c.c.) and ethyl alcohol (50 c.c.). A deep blue colour developed which disappeared after 3 hours' stirring, during which di-[*o*-(*o*′-benzylthiophenylazo)phenyl] disulphide separated; this was collected (1 g., 93%), and crystallisation from benzene gave a yellow-orange solid, m. p. 230—231°, identical with that described above. Acidification of the filtrate with hydrochloric acid precipitated almost pure *2′-benzylthioazobenzene-2-sulphinic* acid (0·4 g., 67%). It crystallised from aqueous alcohol as orange needles, m. p. 125—126° (Found : C, 61·9; H, 4·5; N, 7·5. $C_{19}H_{16}N_2O_2S_2$ requires C, 61·9; H, 4·4; N, 7·6%). (ii) The experiment was repeated, but stirring continued for 20 hr. The yields then were : disulphide, 0·8 g. (74%); sulphinic acid, 0·7 g. (116%).

Action of Sodium Hydroxide on 2′-Benzylthioazobenzene-2-sulphenyl Tribromide (III).—10% Aqueous sodium hydroxide (30 c.c.) was added to a solution of the tribromide (1 g,) in ethyl alcohol (250 c.c.). An immediate red colour developed. After 6 hr. the red solution was acidified with hydrochloric acid. The precipitate of almost pure 2′-benzylthioazobenzene-2-sulphinic acid was filtered off (0·5 g., 78%). It crystallised from aqueous alcohol as orange needles, m. p. 125—126° not depressed by the product obtained by the action of alkali on 2′-benzylthioazobenzene-2-sulphenyl bromide (see above).

o-o′-*Benzylthiophenylazophenyl* p-*Nitrobenzyl Sulphone* (XI).—*p*-Nitrobenzyl bromide (0·6 g.), 2′-benzylthioazobenzene-2-sulphinic acid (0·5 g.), sodium hydroxide (0·07 g.), and ethanol (75 c.c.) were refluxed for 7 hr. On cooling, the *sulphone* crystallised (0·4 g., 58%). Recrystallisation from ethanol gave yellow-orange needles, m. p. 210—212° (Found : C, 62·0; H, 4·2; S, 12·4. $C_{26}H_{21}O_4N_3S_2$ requires C, 61·5; H, 4·1; S, 12·7%).

Action of Hydrobromic acid on 2′-Benzylthioazobenzene-2-Sulphinic Acid (as IX).—The sulphinic acid (0·5 g.), acetic acid (30 c.c.), and 48% hydrobromic acid (10 c.c.) were refluxed for 5 min. After addition of water, 2′-benzylthioazobenzene-2-sulphenyl bromide was extracted with chloroform (0·45 g., 80%; m. p. 180—182° before crystallisation).

o-o′-*Benzylthiophenylazophenyl Methyl Sulphoxide* (X).—2′-Benzylthioazobenzene-2-sulphenyl bromide (0·5 g.), 10% aqueous sodium hydroxide (20 c.c.), and ethanol (50 c.c.) were shaken for 5 min. A deep blue colour developed. Methyl sulphate (3 c.c.) was added, and shaking continued for 30 min. The precipitated *sulphoxide* (0·3 g., 68%) was filtered off and crystallised from ethanol as yellow-orange needles, m. p. 194—195° (sintering at 186°) (Found : C, 66·2; H, 5·0. $C_{20}H_{18}ON_2S_2$ requires C, 65·6; H, 4·9%).

2-Benzylthio-2′-mercaptoazobenzene (XV; R = H).—(i) Sodium sulphide nonahydrate (2 g.) and sodium hydroxide (2 g.) in water (20 c.c.) were added to a solution of di-[*o*-(*o*′-benzylthiophenylazo)phenyl] disulphide (0·3 g.) in benzene (150 c.c.) and ethanol (150 c.c.), and the mixture refluxed for 20 min. The resultant clear red solution was cooled and poured into a separatory funnel containing ice-cold water (100 c.c.). The red aqueous layer was quickly separated from the almost colourless benzene layer, saturated with salt, and acidified with hydrochloric acid. The precipitated yellow 2-benzylthio-2′-mercaptoazobenzene (0·2 g., 66%) was quickly filtered off, washed with water, and dried *in vacuo*. Before drying it melted at 180—184°, and after drying at 204—210°, being readily reoxidised to the original disulphide. When freshly prepared, the thiol was soluble in light petroleum or alcohol and gave a red solution in alcoholic sodium hydroxide. Attempts to recrystallise the crude thiol resulted in formation of the disulphide, m. p. 230—231°. (ii) The experiment was repeated, but the red aqueous layer after separation from benzene was shaken with methyl sulphate (2 c.c.) for 1 hr. Almost pure 2-*benzylthio*-2′-*methylthioazobenzene* separated (0·25 g., 79%). Crystallisation from light petroleum (b. p. 80—100°) gave red-orange needles, m. p. 137—138° (Found: C, 68·8; H, 5·1; S, 17·8. $C_{20}H_{18}N_2S_2$ requires C, 68·6; H, 5·1; S, 18·3%). (iii) Crude, freshly prepared 2-benzylthio-2′-mercaptoazobenzene (0·25 g.) was shaken with ethanol (50 c.c.) and 10% aqueous sodium hydroxide (5 c.c.) for 3 min. The red solution was filtered from some disulphide (0·1 g.) and shaken with methyl sulphate (0·3 c.c.) for 1 hr. The precipitated 2-benzylthio-2′-methylthioazobenzene was collected (0·1 g., 39%). It crystallised from light petroleum (b. p. 60—80°) as orange needles, m. p. 137—138°, undepressed by the product obtained as above.

Copper Complex Salt of 2-*Benzylthio*-2′-*mercaptoazobenzene* (XV; R = ½Cu).—Di-[*o*-(*o*′-benzylthiophenylazo)phenyl] disulphide (0·3 g.) was reduced as described above. The red solution was poured into a separatory funnel containing ice-water and benzene. On acidification with hydrochloric acid, the thiol passed into the benzene layer which was washed with water. 10% Aqueous sodium hydroxide (50 c.c.) and salt (10 g.) were added, and the mixture was shaken for 10 min. The precipitated sodium derivative of 2-benzylthio-2′-mercaptoazobenzene (0·15 g.) was filtered off and redissolved in ethanol (50 c.c.). A dark green *copper complex* separated on addition of a solution of copper sulphate (1 g.) in water (150 c.c.); it was filtered off after 20 hr., dried, and purified by precipitation from solution in chloroform by light petroleum (0·1 g.; m. p. 310—312°) (Found: C, 61·0; H, 4·4; N, 7·3; Cu, 8·4. $C_{38}H_{30}N_4S_4Cu,H_2O$ requires C, 60·6; H, 4·3; N, 7·5; Cu, 8·5%).

2 : 2′-*Di*-(p-*dimethylaminophenylthio*)*azobenzene*.—Dimethylaniline (1·5 c.c.) was added to a suspension of azobenzene-2 : 2′-di(sulphenyl bromide) (0·5 g.) in acetic acid (10 c.c.), and the mixture refluxed for 15 min. There was an immediate reaction, and the red 2 : 2′-*di*-(p-*dimethylaminophenylthio*)*azobenzene* separated. Crystallisation from chlorobenzene yielded a red powder, m. p. 283—285° (Found: C, 68·7; H, 5·6; N, 11·2. $C_{28}H_{28}N_4S_2$ requires C, 69·3; H, 5·8; N, 11·6%).

Action of Zinc on Di-[o-(o′-*bromothiophenylazo*)*phenyl*] *Disulphide* (IV).—The disulphide (0·3 g.), zinc dust (4 g.), and toluene (200 c.c.) were refluxed for 20 min. The mixture was filtered hot and allowed to cool. A yellow precipitate of the *polysulphide* (XIII; $n \geqslant 2$) separated slowly and was collected (0·15 g., 67%; m. p. 266—268°). It is almost insoluble in organic solvents, but crystallised from nitrobenzene–chlorobenzene as an orange powder, m. p. 266—268° (sintering below 200°) [Found: C, 59·7; H, 3·1; N, 11·3. $(C_{12}H_8N_2S_2)n$ requires C, 59·0; H, 3·3; N, 11·5%].

Action of Sodium Hydroxide on the Bisbromothio-disulphide (IV).—Sodium hydroxide (5 g.) in water (200 c.c.) was added to a suspension of the disulphide (IV) (2·7 g.) in ethanol (120 c.c.). A blue colour developed, but disappeared after 20 hours' stirring. A yellow precipitate was collected (1·3 g., 95%). It crystallised from nitrobenzene–chlorobenzene as an orange powder, m. p. 266—268°, identical with the polysulphide described above. Acidification of the filtrate with hydrochloric acid yielded a yellow precipitate (0·6 g.) which on crystallisation from ethanol gave white needles, m. p. 182—183° (becoming red before melting). The *substance* is sparingly soluble in ethanol and dissolves in aqueous sodium hydroxide with an orange-yellow colour (Found: C, 49·7; H, 3·1; N, 9·4. $C_{12}H_8O_3N_2S_2$ requires C, 49·3; H, 2·8; N, 9·6%). The ethanolic mother-liquors contain an easily soluble yellow acid which could not be obtained pure.

2 : 2′-*Dimercaptoazobenzene* (XVI; R = H).—(i) A solution of sodium sulphide nonahydrate (1 g.) in 5% aqueous sodium hydroxide (20 c.c.) was added to a suspension of the polysulphide (XIII) (0·3 g.) in ethanol (20 c.c.), and the mixture refluxed for 3 min. The resultant clear red solution was cooled, saturated with salt, and acidified with hydrochloric acid. The precipitate of the yellow crude 2 : 2′-dimercaptoazobenzene was filtered off and dried (0·2 g., 67%). Attempts to crystallise it failed; *e.g.*, heating it with ethanol yielded the insoluble polysulphide (XIII), m. p. 266—268°. (ii) The experiment was repeated, but the clear red solution was shaken with benzyl chloride (1 c.c.) for 1 hr. The precipitate of almost pure 2 : 2′-dibenzylthioazobenzene was collected (0·37 g., 67%); m. p. 222—223°, not depressed by an authentic sample. (iii) The experiment was repeated, but benzyl chloride was replaced by methyl sulphate (1 c.c.). The precipitate of almost pure 2 : 2′-dimethylthioazobenzene (0·3 g., 89%) crystallised from ethanol as orange needles, m. p. 154—155° (Brand, *Ber.*, 1909, **42**, 3463, gives 154—155°).

(iv) A filtered solution of crude, freshly prepared, dried 2 : 2′-dimercaptoazobenzene (0·2 g.) in ethanol (20 c.c.) and 10% aqueous sodium hydroxide (8 c.c.) was shaken for 20 min. with methyl sulphate (0·8 c.c.). After addition of water, the precipitate of 2 : 2′-dimethylthioazobenzene was filtered off (0·1 g., 56%). It crystallised from ethanol as orange needles, m. p. 154—155°. (v) The experiment was repeated, but methyl sulphate was replaced by benzyl chloride (0·8 c.c.). 2 : 2′-Dibenzylthioazobenzene (0·16 g., 43%) was obtained, having m. p. 222—223° after crystallisation from toluene, not depressed by an authentic sample.

Copper Complex Salt of 2 : 2′-Dimercaptoazobenzene (XVI; R = $\frac{1}{2}$Cu).—A solution of copper sulphate (2 g.) in 1% sulphuric acid (150 c.c.) was added to a filtered solution of freshly prepared, crude 2 : 2′-dimercaptoazobenzene (0·3 g.) in ethanol (50 c.c.) and 10% aqueous sodium hydroxide (10 c.c.). After 24 hr., the black precipitate was filtered off, washed with water and then ethanol, and dried (0·15 g., 40%). The complex *salt* did not melt below 400°, was insoluble in all solvents, and could not be further purified (Found: S, 19·3; Cu, 19·9. $C_{24}H_{16}N_4S_4Cu_2$ requires S, 20·8; Cu, 20·6%).

This investigation has been carried out with the help of a Maintenance Allowance from the Department of Scientific and Industrial Research (to C. E. V.) which is gratefully acknowledged.

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