46. *Studies in the Colour Reactions of Organic Compounds. Part I. The Colour Reactions of Arylthioureas.*

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CERTAIN nitro-substituted arylthioureas (arylthiocarbamides) dissolve in warm concentrated sulphuric acid with the formation of a violet colour (Dyson and George, J., 1924, **125**, 1702). The object of the present investigation has been to ascertain to what extent this colour reaction is general among the aromatic thioureas and to enquire more particularly into its nature.

Each thiourea examined was of the general form A·NH·CS·NHB. Group A always comprised a nitro-group attached to an aryl residue. No colour is produced unless group B is an aromatic residue, and the inclusion of a nitro-group in B, even if attached to an aromatic residue, precludes colour formation (*e.g.*, in 4 : 4′-dinitro-*s*-diphenylthiourea). Further, the nature of the colour produced is dependent on the aromatic group B, but is independent of the orientation of the nitro-group in A, thus pointing to the fact that the production of colour is concerned mainly with group B.

Hofmann (*Ber.*, 1876, **9**, 105, 140; 1882, **15**, 1290; compare also Chattaway, J., 1924, **125**, 1552) showed that thioureas yield a thiocarbimide and the salt of an amine on acid hydrolysis. 4-Nitro-4′-methyl-*s*-diphenylthiourea was therefore dissolved in cold con-

centrated sulphuric acid to give a pale yellow solution, which at 150° turned deep violet. This violet solution, distilled in slightly superheated steam (110°), gave recognisable quantities of *p*-nitrophenylthiocarbimide (m. p. 115°), and the residue, after being made faintly alkaline, gave *p*-toluidine on further distillation in steam, demonstrating that in the presence of concentrated sulphuric acid the reaction

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4Me \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NCS + NH_2{\cdot}C_6H_4Me$$

proceeds to an appreciable extent. No evidence that the reaction proceeds even in part according to $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4Me \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NH_2 + NCS{\cdot}C_6H_4Me$ was obtained, in spite of the singularly characteristic odour of *p*-tolylthiocarbimide, which would ensure the detection of the smallest trace of the compound. It is concluded, therefore, that the colour is due either to *p*-nitrophenylthiocarbimide or to *p*-toluidine, produced by acid hydrolysis of the original compound.

Examination of *p*-nitrophenylthiocarbimide and of *p*-tolylthiocarbimide showed that both dissolved in concentrated sulphuric acid with a deep lemon-yellow colour, which disappeared on warming. Attempts made to obtain a violet colour from these substances by warming their sulphuric acid solutions with traces of other substances—nitrous acid, nitric acid, bromine, chlorine, *p*-toluidine, *p*-nitrosophenol—were unsuccessful.

On the other hand, the treatment of *p*-toluidine with sulphuric acid containing a trace of nitric acid produced a deep purple colour similar to that obtained from 4-nitro-4′-methyl-*s*-diphenylthiourea in sulphuric acid alone. Comparison shows a close similarity between the colours produced with various types of thioureas and those produced by the corresponding amine with sulphuric acid containing a small trace of nitric acid. The table below illustrates this point (*T* denotes the colour obtained with $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NHB$ in warm concentrated sulphuric acid, and *M* the colour obtained with the corresponding amine in concentrated sulphuric acid containing a trace of nitric acid) :

Group B.	*T*.	Corresponding amine.	*M*.
Phenyl	Reddish-brown	Aniline	Reddish-brown
o-Tolyl	Dull purple	*p*-Toluidine	Dull purple
m-Tolyl	Purple-brown	*m*-Toluidine	Brown; purple tinge
p-Tolyl	Violet	*p*-Toluidine	Deep violet
p-Bromophenyl	Purple-red	*p*-Bromoaniline	Purple-red
p-Chlorophenyl	Crimson	*p*-Chloroaniline	Deep red
p-Fluorophenyl	Rose-red	*p*-Fluoroaniline	Rose-red
p-Iodophenyl	Green	*p*-Iodoaniline	Green
p-Anisyl	Blue, turning mauve	*p*-Anisidine	Blue, turning mauve
α-Naphthyl	Blue ⟶ mauve	α-Naphthylamine	Deep blue, turning purple-red
β-Naphthyl	Green ⟶ sepia	β-Naphthylamine	Green ⟶ sepia

Similar colours were produced when symmetrical arylthioureas of the general form $B{\cdot}NH{\cdot}CS{\cdot}NHB$ were dissolved in warm concentrated sulphuric acid containing a minute trace of nitric acid. Three confirmatory points were also elucidated : (1) When a thiourea, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NHB$, is dissolved in warm concentrated sulphuric acid, the solution gives an immediate blue colour with diphenylamine, indicating the presence of free nitric acid. This reaction can be demonstrated in cases such as *N*-*p*-nitrophenyl-*N*′-propylthiourea, which gives no primary colour reaction. (2) Pure sulphuric acid, containing no trace of nitric acid, will give colours on warming with certain amines having a halogen substituent. (3) Certain amines containing a halogen atom (*e.g.*, *p*-bromoaniline) will give a deep violet colour on prolonged boiling alone, indicating oxidation of one part of the amine by halogen obtained during partial decomposition of the remainder.

The evidence leads definitely to the conclusion that the colours produced when thioureas of the type described are warmed with concentrated sulphuric acid are due, first, to the formation of the corresponding amine, and secondly, to the oxidation of this amine by a trace of nitric acid produced from the nitro-group.

The nature of the colouring matter is at present obscure; it is probably an indoaniline compound. There are two ways by which the colour may be developed with an amine. In the first, the amine (0·01 g.) is dissolved in concentrated sulphuric acid (3 ml.), and one drop of *N*/20-nitric acid added; the colour develops at the junction of the two liquids

and, on mixing, spreads through the whole liquid. Alternatively, the amine (0·01 g.) is dissolved in glacial acetic acid (1 ml.), and the solution shaken with one drop of *N*/20-nitric acid and floated on to concentrated sulphuric acid.

In order to prepare many of the required nitro-substituted thioureas it was necessary to ascertain the best conditions for the production of nitro-substituted arylthiocarbimides. The reaction between thiocarbonyl chloride and nitro-substituted aromatic amines, even when dissolved in a large quantity of an inert solvent, always leads to the formation of much *s*-thiourea : $CSCl_2 + 2NO_2{\cdot}R{\cdot}NH_2 \longrightarrow NO_2{\cdot}R{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}R{\cdot}NO_2$. Prolonged agitation of the aqueous solution of the amine hydrochloride, in presence of excess of hydrochloric acid, with thiocarbonyl chloride gave an almost quantitative yield of the nitro-arylthiocarbimide, even in cases where the nitro-group was in a position ortho to the amino-group.

Experimental.

o-Nitrophenylthiocarbimide.—*o*-Nitroaniline (25 g.) was dissolved in hydrochloric acid (500 ml. of 20%) at 50°, and the filtered warm solution agitated with thiocarbonyl chloride (15 g.) for 70 hours. A solid separated, giving 20 g. of yellow flat plates, m. p. 74°, from dilute acetone (Found : S, 17·8. $C_7H_4O_2N_2S$ requires S, 17·77%).

The following compounds were also prepared.

Thiourea.	% S found.	% S calc.	M. p.	Properties.
N-o-Nitrophenyl-*N'*-propyl	13·6	13·4	168°	Small cream prisms
o-Nitro-*s*-diphenyl	11·8	11·7	188	Brilliant golden-yellow plates
2-Nitro-2'-methyl-*s*-diphenyl	11·2	11·15	192	Sheaves of bright yellow needles
2-Nitro-3'-methyl-*s*-diphenyl	11·1	,,	150	Deep golden-yellow needles
2-Nitro-4'-methyl-*s*-diphenyl	11·15	,,	207	Long flat lemon plates
4'-Bromo-2-nitro-*s*-diphenyl	9·0	9·1	210	Small golden-yellow plates
N-o-Nitrophenyl-*N'*-α-naphthyl	10·0	9·9	145	Small olive-green prisms
N-o-Nitrophenyl-*N'*-β-naphthyl	10·05	,,	176	Minute ochre-coloured needles
s-Di-*o*-nitrophenyl	10·1	10·1	160	Orange needles
2 : 3'-Dinitro-*s*-diphenyl	10·1	,,	116	Orange needles
2 : 4'-Dinitro-*s*-diphenyl	10·1	,,	153	Pale yellow needles
N-m-Nitrophenyl-*N'*-propyl	13·5	13·4	119	White prisms
3-Nitro-*s*-diphenyl	11·9	11·7	156	Yellow plates
3-Nitro-2'-methyl-*s*-diphenyl	11·3	11·15	154	Square lemon-yellow prisms
3-Nitro-3'-methyl-*s*-diphenyl	11·3	,,	158	Small yellow prisms
3-Nitro-4'-methyl-*s*-diphenyl	11·0	,,	157	Minute white crystals
3 : 3'-Dinitro-*s*-diphenyl	10·1	10·1	168	Ochre needles
4'-Bromo-3-nitro-*s*-diphenyl	9·2	9·1	173	Pale yellow prisms
2 : 4'-Dichloro-3-nitro-*s*-diphenyl	9·4	9·35	151	Minute white needles
3 : 2'-Dinitro-6-methyl-*s*-diphenyl	9·0	8·8	160	Deep orange needles
N-m-Nitrophenyl-*N'*-α-naphthyl	10·1	9·9	156	Yellow needles
N-m-Nitrophenyl-*N'*-β-naphthyl	10·2	,,	164	Long flat yellow needles
3 : 3'-Dinitro-6'-methyl-*s*-diphenyl	9·7	9·6	136	Deep lemon needles
3 : 4'-Dinitro-6'-methyl-*s*-diphenyl	9·8	,,	158	Microcrystalline orange plates
3 : 4'-Dinitro-*s*-diphenyl	10·2	10·1	172	Minute crystals
3 : 3'-Dinitro-4'-methyl-*s*-diphenyl	9·5	9·6	115	Deep orange-red prisms
3 : 2'-Dinitro-4'-methyl-*s*-diphenyl	9·5	,,	188	Almost white needles
N-p-Nitrophenyl-*N'*-propyl	13·5	13·4	176	Cream-coloured needles
4-Nitro-*s*-diphenyl	11·8	11·7	175	Pale yellow prisms
4-Nitro-2'-methyl-*s*-diphenyl	11·2	11·15	132	Lemon-yellow needles
4-Nitro-3'-methyl-*s*-diphenyl	11·2	,,	135	Pale orange crystals
4-Nitro-4'-methyl-*s*-diphenyl	11·1	,,	165	Clear lemon-yellow needles
4 : 4'-Dinitro-*s*-diphenyl	10·1	10·1	175	Orange-red prisms
4'-Bromo-4-nitro-*s*-diphenyl	9·1	9·1	164	Cream-yellow needles
4'-Chloro-4-nitro-*s*-diphenyl	10·5	10·4	179	Yellow prisms
4-Nitro-4'-methoxy-*s*-diphenyl	10·5	10·5	155	Yellowish plates
N-p-Nitrophenyl-*N'*-α-naphthyl	10·0	9·9	187	Microcrystalline yellow powder
N-p-Nitrophenyl-*N'*-β-naphthyl	10·1	,,	157	Minute yellow needles
4 : 3'-Dinitro-6'-methyl-*s*-diphenyl	9·7	9·6	175	Bright orange prisms
4 : 3'-Dinitro-4'-methyl-*s*-diphenyl	9·6	,,	176	Palest yellow prisms
4 : 4'-Dinitro-6'-methyl-*s*-diphenyl	9·6	,,	181	Long pale yellow needles
4 : 2'-Dinitro-4'-methyl-*s*-diphenyl	9·8	,,	176	Flat yellow needles
4-Nitro-*o*-tolyl	15·1	15·2	140	Small yellow prisms

Thiourea.	% S found.	% S calc.	M. p.	Properties.
N-4-Nitro-*o*-tolyl-*N'*-propyl	12·8	12·6	173	Small cream prisms
5-Nitro-2-methyl-*s*-diphenyl	11·1	11·15	171	Microcrystalline white needles
4'-Bromo-5-nitro-2-methyl-*s*-diphenyl	8·6	8·7	183	White needles
5-Nitro-2 : 2'-dimethyl-*s*-diphenyl	10·8	10·6	149	Yellow needles
5-Nitro-2 : 3'-dimethyl-*s*-diphenyl	10·8	,,	156	Pale yellow micro-needles
5-Nitro-2 : 4'-dimethyl-*s*-diphenyl	10·9	,,	161	Flat yellow needles
N-4-Nitro-*o*-tolyl-*N'*-α-naphthyl	9·6	9·5	191	Small yellow prism
N-4-Nitro-*o*-tolyl-*N'*-β-naphthyl	9·4	,,	154	Crystalline powder
3 : 3'-Dinitro-6 : 6'-dimethyl-*s*-diphenyl	9·4	9·25	162	Very pale yellow needles
N-5-Nitro-*o*-tolyl-*N'*-propyl	12·6	12·6	157	Pale yellow crystals
4-Nitro-2 : 2'-dimethyl-*s*-diphenyl	10·8	10·6	154	Lemon-yellow plates
4-Nitro-2 : 3'-dimethyl-*s*-diphenyl	10·7	,,	152	Large pale yellow prisms
4-Nitro-2 : 4'-dimethyl-*s*-diphenyl	10·9	,,	150	Light yellow needles
N-5-Nitro-*o*-tolyl-*N'*-α-naphthyl	9·6	9·5	166	Yellow needles
N-5-Nitro-*o*-tolyl-*N'*-β-naphthyl	9·55	,,	165	Pale yellow needles
2-Nitro-*p*-tolyl	15·2	15·2	122	Small orange prisms
N-2-Nitro-*p*-tolyl-*N'*-propyl	12·5	12·6	147	Almost white prisms
3-Nitro-4-methyl-*s*-diphenyl	11·3	11·15	152	Cream needles
4'-Bromo-3-nitro-4-methyl-*s*-diphenyl	8·6	8·6	173	Lemon-yellow needles
3-Nitro-2' : 4-dimethyl-*s*-diphenyl	10·7	10·6	147	Minute white needles
3-Nitro-3' : 4-dimethyl-*s*-diphenyl	10·8	,,	152	Pale yellow crystals
3-Nitro-4 : 4'-dimethyl-*s*-diphenyl	10·5	,,	176	Yellow plates
N-2-Nitro-*p*-tolyl-*N'*-α-naphthyl	9·6	9·5	165	White needles
N-2-Nitro-*p*-tolyl-*N'*-β-naphthyl	9·5	,,	212	Yellowish needles
3-Nitro-4-*p*-tolyl	15·3	15·2	138	Yellow crystals
N-3-Nitro-*p*-tolyl-*N'*-propyl	12·8	12·6	144	White prisms
2-Nitro-4-methyl-*s*-diphenyl	11·3	11·15	125	Orange prisms
4'-Bromo-2-nitro-4-methyl-*s*-diphenyl	8·7	8·6	156	Square yellow prisms
2-Nitro-2' : 4-dimethyl-*s*-diphenyl	10·8	10·6	164	Pale yellow prisms
2-Nitro-3' : 4-dimethyl-*s*-diphenyl	10·6	,,	156	Yellow prisms
2-Nitro-4 : 4'-dimethyl-*s*-diphenyl	10·6	,,	162	Pale yellow needles
N-3-Nitro-4-*p*-tolyl-*N'*-α-naphthyl	9·6	9·5	168	Citron-yellow needles
N-3-Nitro-*p*-tolyl-*N'*-β-naphthyl	9·5	,,	159	Ochre-coloured needles
5-Nitro-2-methoxyphenyl	14·3	14·1	—	Orange prisms
N-5-Nitro-2-methoxyphenyl-*N'*-propyl	12·0	11·9	171	Pale yellow needles
5-Nitro-2-methoxy-*s*-diphenyl	10·7	10·6	173	Crystalline pale brown powder
4'-Bromo-5-nitro-2-methoxy-*s*-diphenyl	8·6	8·4	180	Minute, almost white prisms
5-Nitro-2-methoxy-2'-methyl-*s*-diphenyl	10·2	10·1	162	Crystalline pale brown powder
5-Nitro-2-methoxy-3'-methyl-*s*-diphenyl	10·2	,,	168	Pale brown needles
5-Nitro-2-methoxy-4'-methyl-*s*-diphenyl	10·3	,,	162	Microcrystalline yellow powder
3' : 5-Dinitro-2-methoxy-*s*-diphenyl	9·3	9·2	164	Orange prisms
4' : 5-Dinitro-2-methoxy-*s*-diphenyl	9·4	,,	162	Small orange prisms
N-5-Nitro-2-methoxyphenyl-*N'*-α-naphthyl	9·1	9·1	178	Ochre-coloured needles
N-5-Nitro-2-methoxyphenyl-*N'*-β-naphthyl	9·1	,,	175	Flat yellow prismatic needles
5 : 5'-Dinitro-2 : 2'-dimethoxy-*s*-diphenyl	8·6	8·5	175	Brown needles
3-Nitro-*o*-tolyl	15·3	15·15	171	Pale yellow needles
4'-Bromo-2-nitro-6-methyl-*s*-diphenyl	8·7	8·6	164	Pale yellow needles
N-3-Nitro-*o*-tolyl-*N'*-α-naphthyl	9·4	9·5	171	Pale yellow plates
2-Nitro-4' : 6-dimethyl-*s*-diphenyl	10·8	10·6	160	Small yellow needles
4-Nitro-3-methyl-*s*-diphenyl	11·25	11·15	158	Minute prisms
4'-Fluoro-4-nitro-3-methyl-*s*-diphenyl	10·2	10·5	154	Minute, almost white prisms
4'-Bromo-4-nitro-3-methyl-*s*-diphenyl	8·8	8·6	147	Small yellow crystals
N-6-Nitro-*m*-tolyl-*N'*-α-naphthyl	9·7	9·5	142	Minute cream prisms
N-6-Nitro-*m*-tolyl-*N'*-β-naphthyl	9·6	,,	172	Microcrystalline powder
4-Nitro-3 : 4'-dimethyl-*s*-diphenyl	10·8	10·6	110	Pale yellow needles
Thiocarbimide.				
3-Nitro-*o*-tolyl	16·6	16·5	84	Brownish plates
4-Nitro-*o*-tolyl	16·6	,,	74	Pale cream needles
5-Nitro-*o*-tolyl	16·6	,,	92	Lemon-yellow plates
2-Nitro-*p*-tolyl	16·7	,,	68	Clear pale yellow prisms
3-Nitro-*p*-tolyl	16·5	,,	67	Long yellow needles
6-Nitro-*m*-tolyl	16·7	,,	77	Pale yellow plates
5-Nitro-2-methoxyphenyl	15·2	15·2	83	Large prisms

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