CCCCLVII.—*The Inhibitory Effect of Substituents in Chemical Reactions. Part II. The Reactivity of the* iso*Thiocyano-group in Substituted Arylthiocarbimides.*

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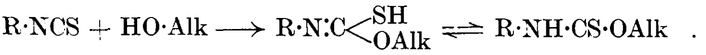
RESULTS of previous experiments (Dyson, George, and Hunter, J., 1927, 436) have shown that the reaction between thiocarbonyl chloride and arylamines is, in general, too rapid to allow of its use as a critical method for the investigation of the effect of substituents on reactivity, and it was therefore decided to examine quantitatively a reaction which could be more easily controlled.

To be of value in this respect the chosen reaction must have the following properties: (1) It must be simple, comparatively free from side reactions, involve only the minimum number of reacting substances, and be as nearly as possible irreversible. (2) It must proceed at a measurable rate. (3) One, at least, of the reacting substances must be capable of comparatively accurate analytical determination. (4) The reaction should proceed entirely in the liquid phase without the separation of solid material. (5) It must take place even when the aryl nucleus is loaded with a variety of substituents.

Among the very few reactions which fulfil these conditions, that most suitable to our purpose was found to be the formation of thiourethanes from aryl-thiocarbimides by prolonged boiling with alcohols :



$$\mathrm{R{\cdot}NCS + HO{\cdot}Alk \longrightarrow R{\cdot}N{:}C{<}^{SH}_{OAlk} \rightleftharpoons R{\cdot}NH{\cdot}CS{\cdot}OAlk} \quad . \quad (A)$$

By using a large excess of alcohol (100—150 mols.) it is possible to observe the formation of the thiourethanes as an almost unimolecular reaction, whilst, save in one or two exceptional cases, no side-reactions were observed to interfere with determinations made upon the main reaction. Moreover, the reaction was not appreciably reversible under the condition of the experiments, although some hours were usually necessary for its completion, except in cases where certain substituents in the nucleus led to considerable acceleration of thiourethane formation. The reaction was not appreciably catalysed or inhibited by the presence of hydrogen ions, identical results being obtained with pure ethyl alcohol and with $N/100$-hydrogen chloride in pure ethyl alcohol. The thiourethanes are easily soluble in hot alcohol, and except in one case no difficulty was experienced from the separation of solid matter.

In the experiments described below, a chemical method was devised for the measurement of the amounts of thiocarbimide remaining in the reaction liquid ; it depended on the rapid combination which takes place between arylamines and thiocarbimides in hot alcoholic solution :

$$\mathrm{R{\cdot}NCS + NH_2R = CS(NHR)_2} \quad . \quad . \quad . \quad (B)$$

The use of aniline as the arylamine in equation (B) led to several inaccuracies, but benzidine reacted rapidly,

$$\mathrm{R{\cdot}NCS + NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2 \longrightarrow R{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2} \quad . \quad . \quad (C)$$

giving thiocarbamides which are only very slightly soluble in cold alcohol (approximately 0·1% at 15°), and can be estimated gravimetrically. This reaction provided the basis for the present experiments.

The velocities of reaction between 75 arylthiocarbimides and ethyl alcohol have been determined, the results of which are discussed below. Phenylthiocarbimide itself reacted comparatively slowly, and in Fig. 1 the broken line indicates the rate of disappearance of the thiocarbimide from an $N/13{\cdot}5$-solution at the b. p. (78·5°) of the alcohol.

Nitro-substituted Arylthiocarbimides.—Except in one case, nitro-substituted arylthiocarbimides reacted with ethyl alcohol too rapidly to admit of quantitative measurement. The approximate time required for the complete conversion of the thiocarbimide into the thiourethane was estimated by observing the amount of the thiocarbamide formed on heating a measured sample with benzidine. The absence of a weighable amount of the thiocarbamide was taken as a sign that the reaction was complete. Nitromesitylthiocarbimide could not be induced to react with ethyl alcohol under the conditions of our experiments. The results with other nitro-substituted arylthiocarbimides are given in Table I, in which the time shown is that (in minutes) required for completion of the reaction between ethyl alcohol and the thiocarbimide in $N/13{\cdot}5$-solution.

TABLE I.

Phenylthiocarbimide.	Time.	Phenylthiocarbimide.	Time.
2-Nitro-	15	3-Nitro-6-methyl-	10
3-Nitro-	20	2-Nitro-3-methyl-	40
4-Nitro-	20	3-Nitro-4-methyl-	20
2-Nitro-6-methyl-	20	3-Nitro-6-methoxy-	30
2-Nitro-4-methyl-	15	3-*Nitro*-4-*fluoro*-	10
4-Nitro-2-methyl-	10	3-Nitro-5-chloro-	15

These results indicate clearly that the nitro-group has a very strong activating influence on the *iso*thiocyano-group, which is independent of the relative positions of the two groups and is not materially diminished by the presence of other groups.

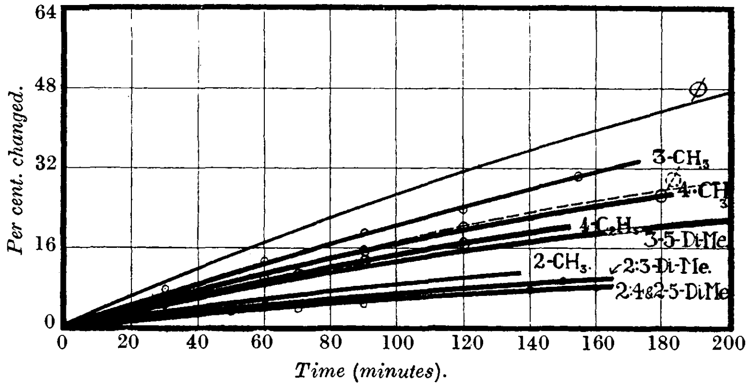
Results obtained with the alkyl-substituted arylthiocarbimides are given in Table II, and are represented diagrammatically in Fig. 1. In this and subsequent tables, x represents the percentage of thiocarbimide which has reacted in 60 minutes.

TABLE II.

Phenylthiocarbimide.	x, %.	Phenylthiocarbimide.	x, %.
2-Methyl-	5·5	3 : 5-Dimethyl-	8
3-Methyl-	12·5	2 : 4 : 6-Trimethyl-	Nil
4-Methyl-	10·5	3 : 4 : 6-Trimethyl-	Nil
2 : 3-Dimethyl-	4·5	4-Ethyl-	9
2 : 4-Dimethyl-	3·5	4-*iso*Propyl-	Nil
2 : 5-Dimethyl-	3·5	6-Methyl-3-*iso*propyl-	Nil
2 : 6-Dimethyl-	Nil	(Unsubstituted)	17

It is clear from these results that the alkyl group as a nuclear substituent inhibits the reaction, and that the inhibition is greatest with an ortho-substituent and least with a meta, the effect of a para-substituent lying between the two. As with the analogous halogen compounds, the effect of the alkyl groups is additive, and in the case of those thiocarbimides containing two nuclear methyl groups the reactivity of the *iso*thiocyano-group is less than that of either of the analogous thiocarbimides containing the methyl group alone. Complete inhibition of the reaction was observed in the case of 2 : 6-dimethylphenylthiocarbimide, and the most highly reactive of these xylylthiocarbimides was observed to be the 3 : 5-dimethyl isomeride. The presence of three methyl groups in the 2 : 4 : 6- or 3 : 4 : 6-positions reduced the reactivity of the group to such an extent that no reaction was discernible. Again, the ethyl group in the para-position exerted a more powerful inhibitory action than the methyl group in the same position, and in the case of the *iso*propyl group, inhibition was complete.

FIG. 1.



Halogen-substituted Arylthiocarbimides.—Halogen atoms in any position in the nucleus of an arylthiocarbimide accelerate the reaction, as shown in Table III. When the halogens are arranged in decreasing order of activating ability, the order I>Br>Cl>F appears, both in meta- and in para-positions. That the effect is approximately additive is shown by the 2 : 4-, 2 : 5-, and 3 : 5-dichlorophenylthiocarbimides, all of which react very rapidly, as though the two atoms were exerting their influences on the *iso*thiocyano-group independently. Graphical representation of this group of thiocarbimides is given in Figs. 2, 3, and 4.

TABLE III.

Phenylthiocarbimide.	x, %.	Phenylthiocarbimide.	x, %.
2-Chloro-	36	4-Fluoro-	40
2-Bromo-	39	4-Chloro-	54
2-Iodo-	Decomp.*	4-Bromo-	60
3-Fluoro-	59	4-Iodo-	62
3-Chloro-	63	2 : 4-Dichloro-	*ca.* 70
3-Bromo-	65	2 : 5-Dichloro-	*ca.* 65
3-Iodo-	67	3 : 5-Dichloro-	*ca.* 100

* Evolution of iodine accompanied decomposition.

Considerable interest attaches to the reactivities of the thiocarbimides which contain both halogen and alkyl groups in the nucleus, since in these cases two types of substituent are acting in opposition to one another. All ten chlorotolylthiocarbimides have been quantitatively examined, together with three highly alkyl-substituted chlorophenylthiocarbimides, the results from

FIG. 2.

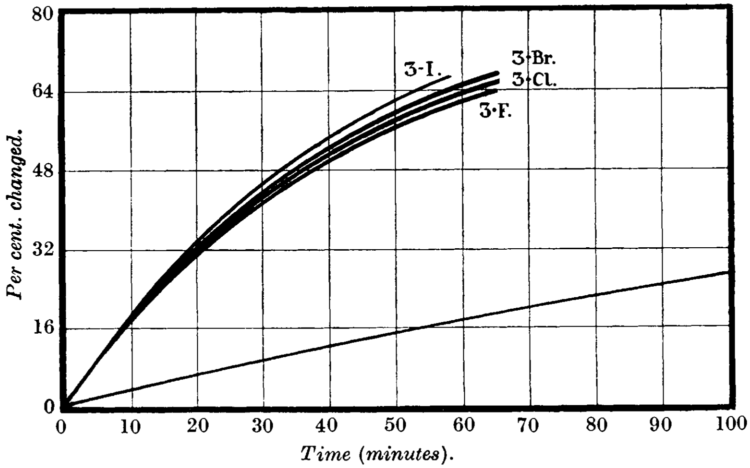
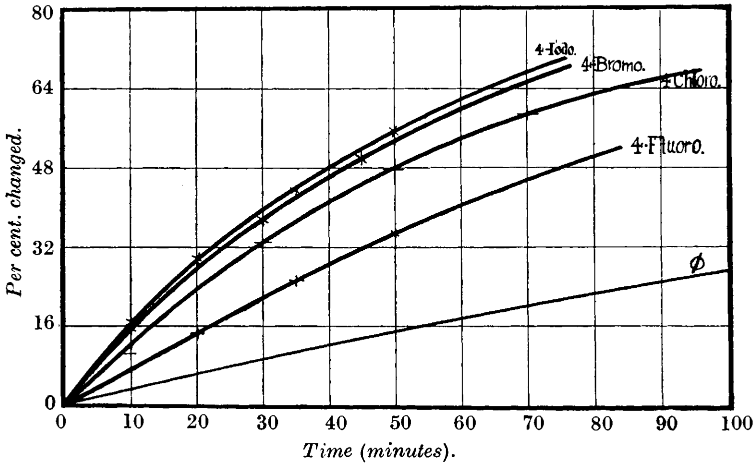


FIG. 3.



these compounds being shown in Table IV, which is divided into three groups, the first related to 3-chlorophenylthiocarbimide, the second to the 4-chloro-, and the third to the 2-chloro-isomeride. Graphs showing the progress of these reactions are given in Figs. 4, 5, and 6.

In the first class, it is clear that the inhibitory action of the methyl group is acting in opposition to the accelerating action of the halogen substituent, with the result that in no case does the reactivity of the *iso*thiocyano-group of the alkyl-substituted chlorophenylthiocarbimides appreciably exceed that of the parent 3-chlorophenyl-

FIG. 4.

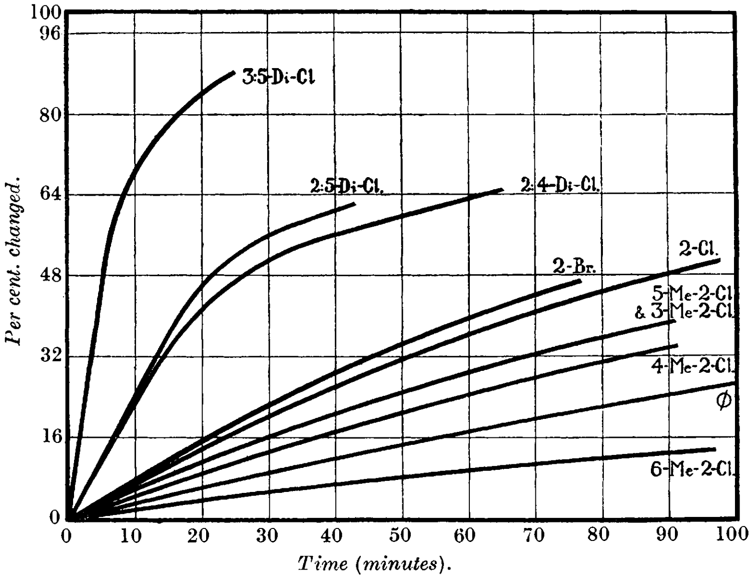
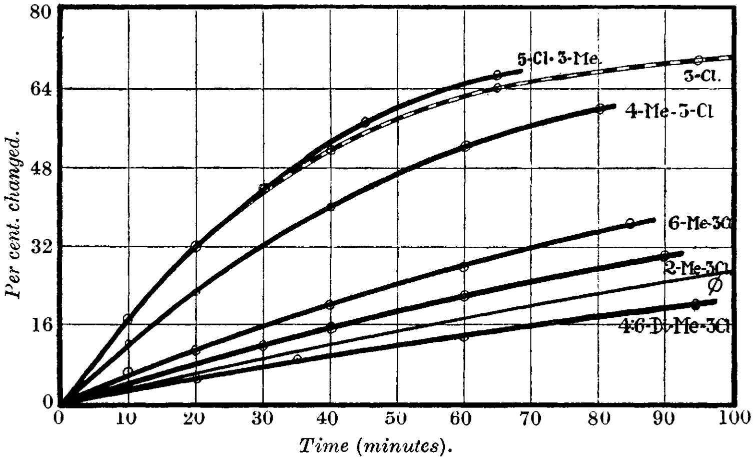


FIG. 5.



thiocarbimide. A methyl group in the 5-position has the least influence on the reactivity of the *iso*thiocyano-group in alkyl-substituted 3-chlorophenylthiocarbimides, which is to be expected from the fact that 3-tolylthiocarbimide is more reactive than either the 2- or the 4-tolyl isomeride. The methyl group in the 4-position exerts a slightly greater inhibitory action, while there is a considerable difference between the reactivities of the two compounds in which the methyl group is in a position ortho to the *iso*thiocyano-group. For instance, 3-chloro-6-methylphenylthiocarbimide is much more reactive than its 2-methyl isomeride, and this difference in activity must, in some way, be due to a "screening" effect of the 2-methyl group, standing between the *iso*thiocyano-group and the chlorine atom.

Fig. 6.

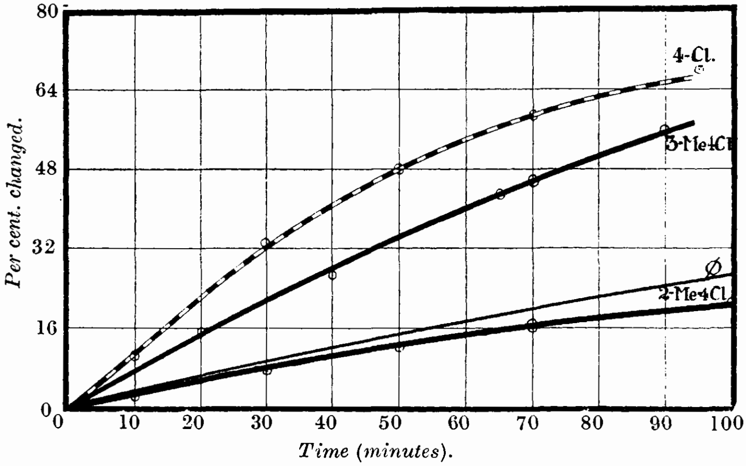


Table IV.

	Phenylthiocarbimide.	x, %.
I.	3-Chloro-	63
	3-Chloro-5-methyl-	65
	3-Chloro-6-methyl-	28
	3-Chloro-4-methyl-	52
	3-Chloro-2-methyl-	23
	3-Chloro-4 : 6-dimethyl-	14
	3-Chloro-2 : 4 : 6-trimethyl-	Nil
II.	4-Chloro-	54
	4-Chloro-2-methyl-	15
	4-Chloro-3-methyl-	40
III.	2-Chloro-	36
	2-Chloro-5-methyl-	29
	2-Chloro-3-methyl-	29
	2-Chloro-4-methyl-	25
	2-Chloro-6-methyl-	10
	2-Chloro-3 : 4 : 6-trimethyl-	Nil

When there are two methyl groups present together in the same nucleus, as in the case of 3-chloro-4 : 6-dimethylphenylthiocarbimide, the reactivity of the *iso*thiocyano-group is lower than when any single methyl group is present. In the case of the 3-chloro-2 : 4 : 6-trimethylphenylthiocarbimide, the accumulated influence of the three methyl groups completely overcomes the accelerative tendency of the 3-chloro-atom, leading to complete inhibition of the reactivity of the *iso*thiocyano-group, under the conditions of the experiment.

In the case of the 4-chloro-compounds, both the 2- and the 3-methylthiocarbimides are less reactive than the parent compound, and the methyl group in the 2-position is a more active inhibiting agent than the corresponding group in the 3-position. In the 2-chloro-compounds, the methyl group in the 5-position is again the least inhibitory, the corresponding group in the 3-position, however, being almost equal in its effect. In the 4-position the effect is slightly more pronounced, the reaction velocity being a little less than with the corresponding compound containing the methyl group in the 3- or the 5-position. When in the 6-position, the methyl group has a maximum effect, and 2-chloro-6-methylphenylthiocarbimide is the least reactive of the monomethyl-substituted 2-chlorophenylthiocarbimides. The complete indifference which 2-chloro-3 : 4 : 6-trimethylphenylthiocarbimide exhibits towards ethyl alcohol at the b. p. indicates, as in the case of the 3-chloro-2 : 4 : 6-trimethyl analogue, that the combined inhibiting influence of the three methyl groups is stronger than the accelerating influence of the chlorine atom.

Alkoxy-compounds.—A series of thiocarbimides of the aromatic series containing a nuclear methoxy- or ethoxy-group was examined, and the reactions with ethyl alcohol were followed. The results so obtained are shown in Table V, their graphical representation being given in Figs. 7 and 8. They indicate that the general trend of reaction velocities, *m*>*o*>*p*, is maintained even when, as in the case of the monomethoxy- and monoethoxy-substituted phenylthiocarbimides, the *m*-compound is more reactive, and the *o*- and the *p*-compound are less reactive, than unsubstituted phenylthiocarbimide. The additive nature of these modifying influences

TABLE V.

Phenylthiocarbimide.	x, %.	Phenylthiocarbimide.	x, %.
2-Methoxy-	4·5	2 : 6-Dimethoxy-	Nil
3-Methoxy-	18·5	3 : 4-Dimethoxy-	19
4-Methoxy-	15·5	3 : 5-Dimethoxy-	27
2-Ethoxy-	3·0	3-Chloro-4-methoxy-	53
3-Ethoxy-	24·0	4-Chloro-3-methoxy-	63
4-Ethoxy-	9·5	5-Chloro-2-methoxy-	16
2 : 5-Dimethoxy-	8·0	5-Chloro-3-methoxy-	80

on the reactivity of the *iso*thiocyano-group is remarkably constant, and is shown by the compounds containing two methoxy-groups in the nucleus. The 3 : 5-dimethoxy-compound is the most reactive, exceeding in this respect the 3-methoxy-compound, whilst the *iso*thiocyano-group of the 2 : 6-dimethoxy-analogue exhibits no reactivity under the conditions of our experiments.

FIG. 7.

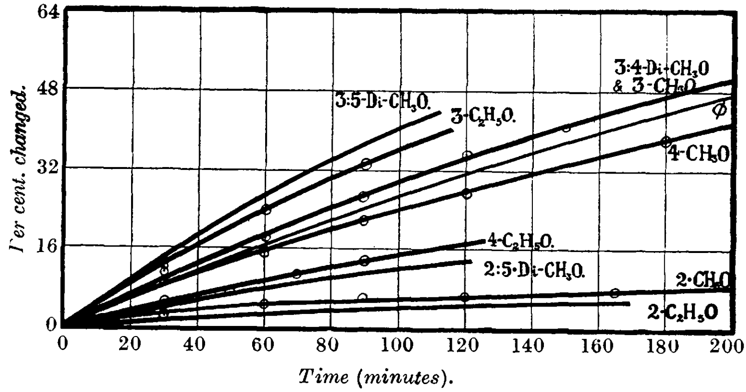
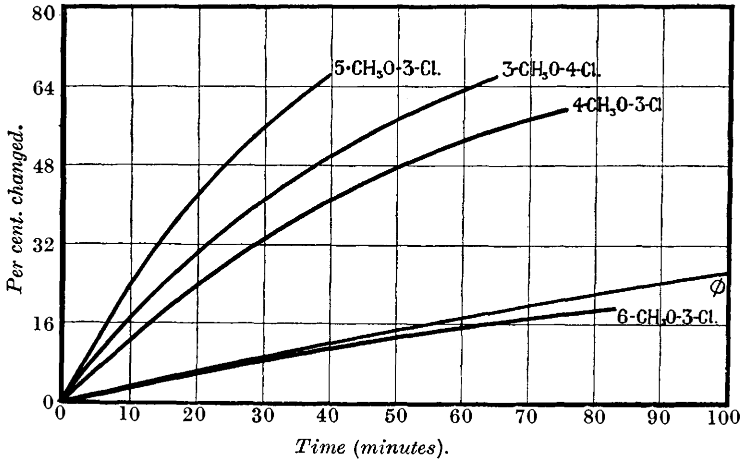


FIG. 8.



With the compounds containing both a chlorine atom and a methoxy-group in the nucleus, the same independence of influence on the reactivity of the *iso*thiocyano-group is evident, as was observed with the corresponding chlorotolyl derivatives.

Discussion of Results.

The results shown above demonstrate that the nuclear substituents have a profound effect on the reactivity of the *iso*thiocyano-group in arylthiocarbimides. Whereas halogen atoms and nitro-groups (and the methoxy- and the ethoxy-group in the *m*-position) accelerate the rate of reaction with ethyl alcohol, alkyl or *o*- and *p*-alkoxyl groups retard the addition. Any explanation of these facts must also account for the following phenomena :

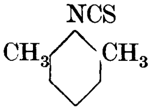
(1) The effect of more than one substituent is approximately the sum of the effects of the substituents acting alone, as, *e.g.*, in the chlorotolyl-, the chloroalkoxy-, and the dichlorophenyl-thiocarbimides.

(2) The *m*-substituted compound is always more reactive than the corresponding *o*- or *p*-substituted compound. This result is independent of whether the compound reacts more readily than phenylthiocarbimide or otherwise. In this connexion, the results obtained with the methoxy- and ethoxy-substituted phenylthiocarbimides are of interest, since they show that the superior reactivity of meta-substituted derivatives is retained even when the reactivity of unsubstituted phenylthiocarbimide lies *between* that of the *m*- and the *p*-substituted compound.

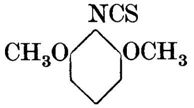
(3) The reactivity varies with the nature of the substituent group, the nitro-group being most active in acceleration, and the *iso*propyl group most active in inhibition.

(4) The anomalous behaviour of the ortho-substituted compounds, which in some cases exhibit the usual phenomena of steric hindrance and in others do not.

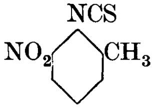
As examples of (4), one may cite 2 : 6-dimethyl- (I), 2 : 6-dimethoxy- (II), and 6-nitro-2-methyl-phenylthiocarbimides (III). In the first two cases the inhibitory effect of the ortho methyl and methoxyl groups is intensified to such an extent that, under the conditions of our experiments, no reaction with ethyl alcohol could be observed; on the other hand, the third thiocarbimide had reacted completely after 20 minutes—almost as rapidly as though no methyl substituent had been present, and considerably faster than in the absence of the nitro-group. This offers an analogy with the facts recorded in Part I of this series, *viz.*, that 2 : 6-xylidine and 2 : 6-dimethoxyaniline react readily with thiocarbonyl chloride, whereas 2 : 6-dinitroaniline is unaffected by this reagent.



(I.)

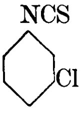


(II.)

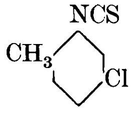


(III.)

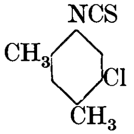
On the other hand, the four 3-chlorophenylthiocarbimides, unsubstituted (IV), 6-methyl- (V), 4 : 6-dimethyl- (VI), and 2 : 4 : 6-trimethyl- (VII), are arranged in order of decreasing reactivity of



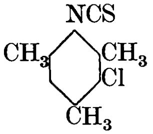
(IV.)



(V.)



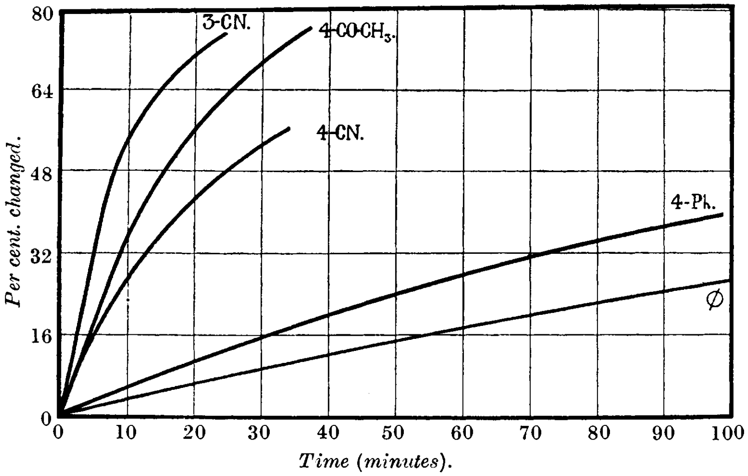
(VI.)



(VII.)

the *iso*thiocyano-group, from which it is clear that the additive effect of substituents, previously referred to, persists when a number of such substituents occupy ortho-positions.

Fig. 9.



In order to ascertain the effect of incorporating into the substituent group, atoms capable of acting as centres of unsaturation, a number of thiocarbimides was examined in which the substituents comprised the carbonyl and the cyano-group. Results obtained with these compounds are given in Table VI.

TABLE VI.

Thiocarbimide.	x, %.	Thiocarbimide.	x, %.
4-Tolyl	10·5	Diphenyl-4	28·5
4-Aldehydophenyl	100	Tolyl	10·5
3-Tolyl	12·5	3-Cyanophenyl	86·5
3-Aldehydophenyl	100	4-Cyanophenyl	66
4-Ethylphenyl	9		
4-Acetylphenyl	89		

Graphical representation of the results obtained with these compounds is given in Fig. 9. No curves are given for the thiocarbimides containing the aldehyde group, since the results were only sufficient to indicate the general trend of the reaction.

In the three pairs of compounds on the left, one member of each pair contains a fully saturated alkyl group, and the other, a similar group in which one methylene group has been replaced by a carbonyl group. Such a group may be considered a centre of unsaturation and as such would be expected to exert a greater activating influence on the *iso*thiocyano-group of the aromatic nucleus than the corresponding alkyl group. If this is true, an increase in the reaction velocity is to be expected: this increase was, in fact, shown to exist and to be very marked.

In the fourth pair the presence of a phenyl group in the para-position also leads to an enhanced reactivity of the *iso*thiocyano-group, presumably due to the presence of unsaturation in the shape of the sextuple group of the substituent nucleus. Finally, the degree of unsaturation associated with the cyano-group led us to expect a very enhanced reaction velocity with aromatic thiocarbimides in which this group was inserted. Such proved to be the case in the last pair.

EXPERIMENTAL.

The method adopted for the determination of the reaction velocity was as follows. The reaction was conducted in a 250-c.c. flask of resistance glass fitted with a reflux condenser, through the inner tube of which a pipette could be inserted for the periodical withdrawal of samples. The calculated quantity of thiocarbimide required to make an $N/13{\cdot}5$-solution in alcohol was weighed out into the flask, the condenser attached, and the flask placed in a water-bath heated to 90°. This temperature sufficed to keep the alcohol in a state of rapid ebullition. When the flask had become warm, boiling ethyl alcohol (100 c.c. measured at 15°) was added through the condenser, the stop-clock started, and 10 c.c. of the well-mixed solution withdrawn immediately and rapidly boiled down to a volume of 3—5 c.c. in a small beaker containing benzidine (0·3 g.). The boiling was continued for exactly 2 minutes, although in many cases the bulk of the precipitate of benzidinethiocarbamide had formed after 15 seconds. After standing for 12 hours, the whole was evaporated to dryness in the steam-oven, kept at 100° for 6 hours, and any excess of benzidine removed by standing for 12 hours with cold absolute alcohol (15 c.c.). The thiocarbamide was then filtered off through a tared Gooch crucible and washed slowly with a known volume of alcohol, the temperature of which had been adjusted to 15°: the exact quantity used varied with the character of the precipitate to be washed, but remained constant for any set of experiments on the same reaction—usually 10 c.c. of wash-liquid were used, the total volume of filtrate and washings being 25 c.c. The crucible was heated at 100° for $1\frac{1}{2}$ hours, and weighed after cooling in a desiccator over sulphuric acid. In cases where a very small amount of precipitate had to be weighed, a tared crucible was used containing about 0·2 g. of the same benzidinethiocarbamide from a previous estimation, in order that the same solubility correction might be made throughout the series.

The solubility correction was calculated during the earlier experiments in two ways : (1) by observing the loss in weight of a tared crucible containing 0·2 g. of the thiocarbamide under investigation when 25 c.c. of alcohol at 15° were passed through it at a rate similar to that used in washing the precipitates obtained in the actual experiments, the solubility being calculated on the assumption that the filtrate and washings were completely saturated; and (2) by determining the solubility of the precipitate in alcohol in the usual way, and calculating the solubility correction on the assumption that filtrate and washings were both saturated. The two results agreed well, and in later experiments only the latter method was used.

The numerical results are given in Table VII; one result, *viz.*, that with 4-chlorophenylthiocarbimide, is given below in full, but in the others the weighings are not recorded. The values are in most cases the means of several determinations.

Detailed results with 4-chlorophenylthiocarbimide. The pure thiocarbimide (1·2555 g.) was treated as described above. The benzidinethiocarbamide was soluble in alcohol to the extent of 0·188 g./litre at 15°. The filtrate and washings in each case amounted to 25 c.c.

Time, mins.	Wt. with ppt., g.	Wt. without ppt., g.	Ppt.	Ppt. corr. for solubility.	x, %.
0	16·7505	16·5465	0·2040	0·2087	0
10	17·3115	17·1295	0·1820	0·1867	10·6
30	14·7215	14·5846	0·1350	0·1397	33·1
50	15·5115	15·4075	0·1040	0·1087	47·9
70	16·3050	16·2240	0·0810	0·0857	58·9
95	15·7830	15·7210	0·0620	0·0667	68·0

$k = 2{\cdot}17 \times 10^{-4}$, the reaction being assumed pseudo-unimolecular.

Materials.—Ethyl alcohol. The pure alcohol of commerce was boiled under reflux for 2 days with stick potassium hydroxide and distilled on to quicklime, over which it was kept for 24 hours. It was filtered from the lime and fractionally distilled, the fraction of b. p. 78—79° being collected. To the alcohol so prepared, 2·5% of water was added, since it was desired to eliminate any errors which might arise from the hygroscopic nature of absolute alcohol.

TABLE VII.

Thiocarbimide.	$k \times 10^4$.	Proportion converted into thiourethane at time t (mins.).									
		t.	x, %.	t.	x, %.	t.	x, %.	t.	x, %.	t.	x, %.
Phenyl	0·524	10	3·4	30	7·8	50	14·3	75	20·3	100	26·2
2-Tolyl	0·144	10	1·0	20	1·8	40	3·2	65	5·4	95	7·15
3-Tolyl	0·385	30	7·4	60	13·1	90	18·9	120	23·7	155	30·5
4-Tolyl	0·297	30	5·7	60	9·4	90	15·1	130	20·6	180	26·5
2 : 3-Dimethylphenyl	0·113	10	0·5	30	2·6	60	4·0	90	5·4	150	8·9
2 : 4-Dimethylphenyl	0·092	10	1·2	30	1·8	50	2·6	70	3·5	90	4·5
2 : 5-Dimethylphenyl	0·092	10	0·4	30	—	60	2·3	90	4·3	120	7·4
2 : 6-Dimethylphenyl	—	No reaction.									
3 : 5-Dimethylphenyl	0·222	30	5·9	65	9·7	90	12·6	120	15·3	180	21·4
2 : 4 : 6-Trimethylphenyl	—	No reaction.									
3 : 4 : 6-Trimethylphenyl	—	No reaction.									
4-Ethylphenyl	0·259	10	1·6	30	4·6	50	7·5	70	10·3	90	13·1
4-*iso*Propylphenyl	—	No reaction.									
6-Methyl-3-*iso*propylphenyl	—	No reaction.									
2-Chlorophenyl	1·24	10	6·9	30	19·7	50	31·6	70	40·8	95	49·1
2-Bromophenyl	1·40	10	7·8	20	15·9	35	26·2	55	36·4	75	43·35
2-Iodophenyl	—	Decomposed.									
3-Chlorophenyl	2·99	10	17·7	20	32·6	40	51·6	65	64·3	95	70·35
3-Fluorophenyl	2·88	10	16·5	20	29·35	30	41·3	45	53·0	60	62·9
3-Bromophenyl	3·09	10	17·5	20	33·7	30	43·1	45	56·2	60	63·5
3-Iodophenyl	3·31	10	18·9	20	34·6	30	45·9	40	55·3	50	62·2
4-Fluorophenyl	1·41	10	6·8	20	14·6	35	25·1	50	34·7	70	44·7
4-Chlorophenyl	2·17	10	10·6	30	33·1	50	47·9	70	58·9	95	68·0
4-Bromophenyl	2·58	10	16·3	20	28·7	30	38·0	45	50·6	65	63·35
4-Iodophenyl	2·74	10	17·0	20	29·7	35	44·3	50	54·8	70	63·6
2 : 4-Dichlorophenyl	4·10	10	22·6	25	45·1	35	54·6	50	59·5	65	63·9
2 : 5-Dichlorophenyl	4·62	10	23·9	20	47·1	30	53·8	45	57·7		
3 : 5-Dichlorophenyl	17·9	10	69·3	20	84·2						
3-Chloro-5-methylphenyl	3·04	10	17·5	20	31·7	30	44·0	45	57·0	60	65·55
3-Chloro-6-methylphenyl	0·92	10	6·5	20	10·8	40	20·0	60	28·0	85	36·95
3-Chloro-4-methylphenyl	2·08	10	12·2	20	22·3	40	40·0	60	52·4	80	60·0
3-Chloro-2-methylphenyl	0·682	10	3·4	30	11·7	60	21·5	90	28·9		
3-Chloro-4 : 6-dimethylphenyl	0·411	10	3·3	20	6·0	35	8·9	60	13·3	95	19·3
3-Chloro-2 : 4 : 6-trimethylphenyl	—	No reaction.									
4-Chloro-2-methylphenyl	0·44	10	2·3	31	7·5	50	12·1	70	16·3	100	22·0
4-Chloro-3-methylphenyl	1·41	10	9·4	20	15·1	40	28·4	65	42·5	95	55·9
2-Chloro-5-methylphenyl	0·948	10	6·0	20	11·35	40	19·9	60	28·5	80	34·9
2-Chloro-3-methylphenyl	0·948	10	5·7	20	10·3	40	20·0	60	28·75	90	38·3
2-Chloro-4-methylphenyl	0·778	10	3·9	20	8·3	40	16·8	60	24·0	90	33·3
2-Chloro-6-methylphenyl	0·278	10	0·7	20	2·9	40	6·2	65	8·9	95	13·8
2-Bromo-4-methylphenyl		10	7·7	20	12·9	40	26·4	60	35·1	85	43·9
2-Chloro-3 : 4 : 6-trimethylphenyl	—	No reaction.									
2-Methoxyphenyl	0·099	30	1·6	60	4·5	90	5·7	120	6·7	165	7·1
3-Methoxyphenyl	0·582	30	11·2	60	18·4	90	26·9	120	35·3	150	41·4
4-Methoxyphenyl	0·462	30	9·6	60	15·1	90	21·9	120	27·3	180	38·3
2-Ethoxyphenyl	0·065	10	1·0	40	1·6	65	2·3	95	3·5		
3-Ethoxyphenyl	0·754	10	3·7	60	11·8	60	23·15	90	33·3		
4-Ethoxyphenyl	0·273	10	1·9	30	6·5	50	9·0	70	12·8	90	15·1
2 : 5-Dimethoxyphenyl	0·215	10	3·2	20	4·2	35	5·9	50	7·5	75	8·6
2 : 6-Dimethoxyphenyl	—	No reaction.									
3 : 4-Dimethoxyphenyl	0·582	10	2·8	30	9·1	50	15·8	70	21·7		
3 : 5-Dimethoxyphenyl	0·856	10	18·1	30	41·7	50	59·9	70	71·4	90	80·0
3-Chloro-4-methoxyphenyl	2·14	10	12·0	20	23·0	35	36·9	50	47·4	75	57·9
4-Chloro-3-methoxyphenyl	2·91	10	18·1	30	40·6	60	61·6				
5-Chloro-2-methoxyphenyl	0·467	10	1·5	20	4·8	40	10·9	60	15·3	80	17·3
5-Chloro-3-methoxyphenyl	4·57	10	23·9	20	42·2	30	55·3				
4-Acetylphenyl	6·84	10	33·9	20	55·6	35	74·9	50	85·5	70	92·4
Diphenyl-4	0·896	10	5·5	30	15·0	50	22·1	70	30·1	140	50·0
3-Cyanophenyl	11·1	10	54·3	20	70·9	30	73·4	40	78·8		
4-Cyanophenyl	4·81	10	27·5	20	41·3	30	47·9	50	55·7		

Experiments with alcohol containing 0·1 and 2·5% of water showed that the presence of the latter had no material influence on the rate of reaction. All traces of substances such as pyridine must be rigorously excluded from alcohols used for the determination of rates of reaction, since both primary and secondary amines and cyclic nitrogen bases cause acceleration. This is particularly true of diethylamine, a fact which accounts for the difficulty observed by us in condensing diethylamine itself with arylthiocarbimides in alcoholic solution (Dyson and Hunter, *Rec. trav. chim.*, 1926, **45**, 421; Hunter, *Chem. News*, 1925, **130**, 338). Further, when alkylthiocarbimides are condensed with arylamines, a similar, but less marked, loss of yield due to thiourethane formation is attained when the reaction is conducted in ethyl-alcoholic solution.

The following methods were used for the preparation of the thiocarbimides required for this work. Where no method is stated that used was identical with the method described by Dyson and George (J., 1924, **125**, 1702).

4-*Nitrophenylthiocarbimide*. *p*-Nitroaniline (17 g.) was thoroughly stirred with 10% hydrochloric acid (700 c.c.) and filtered. The filtrate was mechanically shaken in a stoppered bottle with thiocarbonyl chloride (15 g.) for 2 days. The crude thiocarbimide separated as a yellow powder, which, recrystallised from acetone, formed pale yellow needles, m. p. 112°; yield 21 g.

3-*Nitrophenylthiocarbimide*. This was prepared in the same manner: pale yellow needles, m. p. 60°, from acetone.

3-*Nitro*-o-*tolylthiocarbimide*. 3-Nitro-*o*-toluidine (15 g.) was dissolved in diluted hydrochloric acid (1 : 1; 700 c.c.) and shaken with thiocarbonyl chloride (15 g.) for two days. The thiocarbimide separated in deep yellow crystals, and recrystallised from acetone as yellow plates, m. p. 70°; yield 17 g.

4-*Fluoro*-3-*nitrophenylthiocarbimide*. 4-Fluoro-3-nitroaniline (6·7 g.) was dissolved in 2*N*-hydrochloric acid (200 c.c.), and the solution shaken with thiocarbonyl chloride (7 g.) for 24 hours. The *thiocarbimide* separated as a yellow solid which on recrystallisation (with difficulty) from acetone yielded pale yellow plates, m. p. 55°; yield 7 g. (Found: S, 16·24. $C_7H_3O_2N_2FS$ requires S, 16·16%).

4-*Ethylphenylthiocarbimide*. *p*-Aminoethylbenzene (14 g.) was dissolved in chloroform (200 c.c.), and the solution gradually added to a suspension of thiocarbonyl chloride (15 g.) in water (300 c.c.). The mixture was stirred for 1½ hours, the chloroform layer separated, the solvent evaporated, and the residue purified by distillation in steam. The 4-ethylphenylthiocarbimide formed a colourless oil, b. p. 245°, possessing a sharp smell; yield 14 g.

4-*Ethylphenylthiocarbamide*. The foregoing thiocarbimide (2 g.) was heated under reflux with saturated alcoholic ammonia (50 c.c.) for one hour. The solution was poured into water, and the solid filtered off and recrystallised from alcohol; small colourless needles, m. p. 138° (Found: S, 17·9. $C_9H_{12}N_2S$ requires S, 17·8%).

4-iso*Propylphenylthiocarbimide*. This was prepared from *p*-amino*iso*propylbenzene in exactly the same way as the ethyl compound; it is a colourless, highly refracting oil, b. p. 252°. The corresponding *thiocarbamide*, obtained by the action of alcoholic ammonia on the thiocarbimide, formed small white needles, m. p. 134° (Found : S, 16·4. $C_{10}H_{14}N_2S$ requires S, 16·5%).

3-*Fluorophenylthiocarbimide.* *m*-Fluoroaniline, prepared by the method of Ingold and Vass (J., 1929, 421), was converted into the corresponding thiocarbimide by addition to twice its weight of thiocarbonyl chloride suspended in water, vigorous stirring being maintained throughout the addition. The purified, steam-distilled thiocarbimide boiled at 226—227°, and was characterised by conversion into the two thiocarbamides described below.

3-*Fluorophenylthiocarbamide.* The thiocarbimide (2 g.) was gently heated under reflux with saturated alcoholic ammonia (40 c.c.) for ½ hour. The solution was diluted with water until a faint turbidity was produced, and allowed to cool. Crystals of the *thiocarbamide* separated. They were recrystallised twice from dilute alcohol, being finally obtained as small white prisms, m. p. 116° (Found : S, 20·9. $C_7H_7N_2SF$ requires S, 20·5%).

s-*Di*-(3-*fluorophenyl*)*thiocarbamide.* The same thiocarbimide (3 g.) was gently refluxed in benzene solution (30 c.c.) with *m*-fluoroaniline (3 g.) for ½ hour. On cooling, crystals of the *thiocarbamide* separated, and two recrystallisations from alcohol yielded pearly laminæ, m. p. 144° (Found : S, 12·4. $C_{13}H_{10}N_2SF_2$ requires S, 12·12%).

4-*Fluorophenylthiocarbimide.* This was prepared in exactly the same way as the preceding thiocarbimide; it was a colourless oil, m. p. 12°, b. p. 228°, and was characterised by conversion into the following compound.

s-*Di*-(4-*fluorophenyl*)*thiocarbamide*, glistening plates from dilute alcohol, m. p. 145° (Found : S, 12·3. $C_{13}H_{10}N_2SF_2$ requires S, 12·12%), shows the same optical phenomena (thin-film colours) during recrystallisation as does the diphenyl compound (thiocarbanilide).

The dichlorophenylthiocarbimides were prepared by the method of Dyson, George, and Hunter (J., 1926, 3041).

5-*Chloro*-o-*tolylthiocarbimide.* 5-Chloro-*o*-toluidine (6 g.; prepared from 6-nitro-*m*-toluidine by diazotisation, treatment with cuprous chloride, and reduction of the resulting nitro-compound with tin and hydrochloric acid) was dissolved in 80 c.c. of chloroform, and the solution added to a suspension of thiocarbonyl chloride (7 g.) in water (200 c.c.), vigorous stirring being maintained for one hour. The chloroform layer was removed, washed, freed from chloroform, and the residual oil distilled in steam, and fractionated under reduced pressure. 5-Chloro-*o*-tolylthiocarbimide was obtained as a white crystalline solid, m. p. 36°, after recrystallisation. It was characterised by conversion into the following compound.

α-(5-*Chloro*-o-*tolyl*)-β-(β-*naphthyl*)*thiocarbamide*. 5-Chloro-*o*-tolylthiocarbimide (1 g.) was boiled for a few minutes with a benzene solution of β-naphthylamine (1 g. in 15 c.c.). On cooling, a white solid separated, which, on recrystallisation from alcohol, gave minute, white, felted needles of the required *thiocarbamide*, m. p. 163° (Found: S, 9·8. $C_{18}H_{15}N_2SCl$ requires S, 9·8%).

6-*Chloro*-m-*tolylthiocarbimide*. Prepared by a process exactly analogous to that described under 5-chloro-*o*-tolylthiocarbimide, this compound was purified by vacuum distillation, the fraction of b. p. 144—146°/2 mm. being collected. After distillation in steam, 6-chloro-*m*-tolylthiocarbimide was obtained as a pale yellow oil, b. p. 270°. It was characterised by conversion into the following compound.

α-(6-*Chloro*-m-*tolyl*)-β-(β-*naphthyl*)*thiocarbamide*, prepared in exactly the same way as the 5-chloro-*o*-tolyl derivative, forms shining plates, m. p. 154°, from alcohol (Found: S, 9·7. $C_{18}H_{15}N_2SCl$ requires S, 9·8%).

6-*Chloro*-o-*tolylthiocarbimide*. This compound was prepared (yield 8 g.) as a pale yellow oil of penetrating odour, b. p. 276°, from 6-nitro-*o*-toluidine (15 g.) by a process exactly analogous to that described under 5-chloro-*o*-tolylthiocarbimide. It was characterised by conversion into the following compound.

α-(6-*Chloro*-o-*tolyl*)-β-(β-*naphthyl*)*thiocarbamide*. The thiocarbimide (1 g.) was boiled with a benzene solution of β-naphthylamine (0·8 g. in 15 c.c.) for a few minutes. On cooling, minute crystals of the desired *thiocarbamide* separated, and on recrystallisation from alcohol, the compound was obtained in colourless granular crystals, m. p. 150° (Found: S, 9·7. $C_{18}H_{15}N_2SCl$ requires S, 9·8%).

5-*Chloro*-m-*tolylthiocarbimide*. 5-Chloro-*m*-toluidine was first prepared as follows. 5-Nitro-*o*-toluidine (35 g.) was dissolved in hydrochloric acid (250 c.c. each of concentrated acid and water) and warmed to 40° until a clear solution was obtained. To this solution was added potassium chlorate (9·5 g. dissolved in 200 c.c. of water). During the last part of the addition, 3-chloro-5-nitro-*o*-toluidine separated in long, golden-orange needles which, when recrystallised, once from glacial acetic acid and once from alcohol, had m. p. 169°. This compound (18 g.) was suspended in alcohol (120 c.c.), a thin paste being obtained. Sulphuric acid (8 c.c.) was added, followed by sodium nitrite (7 g.). The mixture was warmed on the water-bath, and both aldehyde and nitrogen were evolved. When the evolution of nitrogen had ceased, the alcohol was removed on the water-bath, and the residual matter distilled in steam. 5-Chloro-3-nitrotoluene passed over as a pale yellow oil which solidified in the receiver to a cake. After recrystallisation from alcohol, it was obtained in pale yellow needles, m. p. 59°. Reduction with tin and hydrochloric acid in the usual way yielded 5-chloro-*m*-toluidine, and thence by reaction with thiocarbonyl chloride 5-chloro-*m*-tolylthiocarbimide was obtained in exactly the same way as already described for the 5-chloro-*o*-tolyl analogue. 5-Chloro-*m*-tolylthiocarbimide forms colourless glistening plates, with a faint pleasant smell, m. p. 34°. It was characterised by conversion into the following compound.

α-5-*Chloro*-m-*tolyl*-β-p-*tolylthiocarbamide*. The thiocarbimide (1 g.) was boiled for a few minutes with a benzene solution of *p*-toluidine (0·6 g. in 15 c.c.). On cooling, the *thiocarbamide* separated as a colourless crystalline mass; recrystallisation from alcohol yielded colourless, silky needles, m. p. 156° (Found: S, 10·98. $C_{15}H_{15}N_2SCl$ requires S, 11·02%).

3-*Chloro*-o-*tolylthiocarbimide*. 3-Chloro-*o*-nitrotoluene, prepared by the method of Gibson, Johnson, and Elson (J., 1929, 2735), was reduced to the corresponding 3-chloro-*o*-toluidine with tin and hydrochloric acid, and converted into 3-chloro-*o*-tolylthiocarbimide by reaction with thiocarbonyl chloride in the manner heretofore described. The thiocarbimide forms a pale yellow oil, with a pungent smell, b. p. 269°; it was characterised by conversion into α-3-*chloro*-o-*tolyl*-β-p-*tolylthiocarbamide* by exactly the same procedure as for the corresponding 5-chloro-*m*-tolyl analogue: this forms colourless prismatic needles, m. p. 180° (Found: S, 11·1. $C_{15}H_{15}N_2SCl$ requires S, 11·02%).

4-*Chloro*-o-*tolylthiocarbimide*. The corresponding amine, 4-chloro-*o*-toluidine, was readily prepared from *o*-nitro-*p*-toluidine, and was treated with thiocarbonyl chloride as usual. The thiocarbimide forms a pale yellow oil, b. p. 268°, possessing a penetrating smell, and was characterised by conversion into the following compound. When it (2 g.) was heated under reflux with a saturated alcoholic solution of ammonia (20 c.c.) for ½ hour and then poured into water, it yielded 4-*chloro*-o-*tolylthiocarbamide* as a white solid, which, when filtered off and recrystallised from alcohol, separated in large colourless plates, m. p. 138° (Found: S, 16·0. $C_8H_9N_2SCl$ requires S, 15·9%).

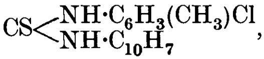
2-*Chloro*-p-*tolylthiocarbimide*, prepared as a pale yellow oil, b. p. 263°, from 4-nitro-*o*-toluidine by a process analogous to that described for 5-chloro-*o*-tolylthiocarbimide, was characterised by conversion as in preceding cases into α-(2-*chloro*-p-*tolyl*)-β-(β-*naphthyl*)*thiocarbamide*, colourless shining plates from alcohol, m. p. 149°, (Found: S, 9·7. $C_{18}H_{15}N_2SCl$ requires S, 9·8%).

6-*Chloro*-m-*xylylthiocarbimide*. 4 : 6-Dinitro-*m*-xylene was reduced by alcoholic ammonium sulphide to 4-nitro-*m*-6-xylidine, orange plates, m. p. 123°. By diazotisation and treatment with cuprous chloride, this compound gave 6-chloro-4-nitro-*m*-xylene, a pale yellow oil resembling nitrobenzene in odour, b. p. 242°. Reduced with activated iron, the nitro-compound gave 6-chloro-*m*-4-xylidine, in shining white plates, m. p. 99°. The 6-chloro-*m*-xylylthiocarbimide was obtained by dissolving this xylidine (10 g.) in chloroform (100 c.c.) and gradually adding the solution to a vigorously stirred suspension of thiocarbonyl chloride (15 g.) in water (200 c.c.). After 2 hours' stirring, the emulsion was broken up by filtration, the chloroform layer freed from solvent, and the residual oil distilled in steam. 6-Chloro-*m*-xylylthiocarbimide is a pale yellow oil, b. p. 278°. It was characterised by conversion into the following thiocarbamide.

α-(6-*Chloro*-m-*xylyl*)-β-(β-*naphthyl*)*thiocarbamide*. Prepared by heating under reflux equimolecular proportions of β-naphthylamine and the foregoing thiocarbimide, dissolved in benzene, this *thiocarbamide* formed small colourless needles, m. p. 154° (Found : S, 9·45. $C_{19}H_{17}N_2SCl$ requires 9·4%).

Chloromesitylthiocarbimide, $C_6HMe_3Cl{\cdot}NCS$ (1 : 3 : 5 : 2 : 4). Nitromesidine (30 g.) was dissolved in hydrochloric acid (300 c.c. of commercial acid; 150 c.c. of water), and heated to 100°, then rapidly cooled and stirred. The suspension of the hydrochloride so obtained was diazotised at −5° with sodium nitrite (14 g.) in water (30 c.c.). The clear diazonium solution was poured into a solution of cuprous chloride (50 g.) in concentrated hydrochloric acid (200 c.c.) at 0°. The chloronitromesitylene was separated by distillation with steam, and formed pale yellow needles, m. p. 59°; yield 28 g. When reduced by tin and hydrochloric acid in the usual way, it gave 21 g. of chloromesidine as a white crystalline mass, m. p. 28°. This was converted into chloromesitylthiocarbimide by a process analogous to that described under 5-chloro-*o*-tolylthiocarbimide. Purification was effected by heating in a current of steam, in which the thiocarbimide is only very slightly volatile, and recrystallising the residue from light petroleum (b. p. 40—50°). In this way, the thiocarbimide was obtained as colourless needles, m. p. 44°. It was characterised by conversion into α-*chloromesityl*-β-(β-*naphthyl*)-*thiocarbamide* in a manner exactly analogous to that described under the corresponding chloro-*m*-xylyl compound. The thiocarbamide formed shining needles, m. p. 181° (Found : S, 8·9. $C_{20}H_{19}N_2SCl$ requires S, 9·0%).

4-*Chloro*-m-*tolylthiocarbimide*. From 3-nitro-*p*-toluidine by a process exactly similar to that detailed under 5-chloro-*o*-tolylthiocarbimide, this was obtained as a very pale yellow liquid with a faint smell of mushrooms, b. p. 272°. α-4-*Chloro*-m-*tolyl*-β-



(β-*naphthyl*)*thiocarbamide*, $CS\begin{matrix}\diagup NH\cdot C_6H_3(CH_3)Cl \\ \diagdown NH\cdot C_{10}H_7\end{matrix}$, small glistening needles, has m. p. 158° (Found : S, 9·9. $C_{18}H_{15}N_2SCl$ requires S, 9·8%).

The following compounds were prepared in an analogous manner.

2-Chloro-*m*-tolylthiocarbimide, a pale yellow oil, b. p. 264°.

α-(2-Chloro-*m*-tolyl)-β-(β-naphthyl)thiocarbamide, colourless needles, m. p. 172°.

3-*Chloro*-p-*tolylthiocarbimide.* The preparation of the requisite 3-chloro-*p*-toluidine presented considerable difficulty. Finally, it was obtained by the chlorination of aceto-*p*-toluidide in glacial acetic acid with a very slow current of chlorine at room temperature, until the theoretical increase in weight had been obtained; the material obtained by pouring this reaction mixture into cold water was hydrolysed with 50% caustic alkali, and the chlorotoluidine isolated by distillation in steam and fractionation of the distillate. 3-Chloro-*p*-tolylthiocarbimide was prepared in the manner already described under 5-chloro-*o*-tolylthiocarbimide and obtained as a colourless oil, b. p. 258°. It was characterised by conversion into α-3-*chloro*-p-*tolyl*-β-p-*tolylthiocarbamide*, lustrous white needles, m. p. 160° (Found : S, 11·00. $C_{15}H_{15}N_2SCl$ requires S, 11·02%).

5-*Chloro*-ψ-*cumene*-6-*thiocarbimide*, $C_6HMe_3Cl\cdot NCS$ (1 : 2 : 4 : 5 : 6). ψ-Cumidine (50 g.) was acetylated, and the acetyl compound nitrated in strong sulphuric acid solution to give 6-nitroaceto-ψ-cumidide (44 g.), pale yellow needles, m. p. 201°. This was hydrolysed to 6-nitro-ψ-cumidine by 4 hours' heating on a water-bath with 50% sulphuric acid (400 c.c.). The base was not isolated, but the solution of its sulphate was cooled, diazotised, and added to a solution of cuprous chloride in concentrated hydrochloric acid. The 6-nitro-5-chloro-ψ-cumene separated as a yellow crystalline solid, m. p. 53°, which was volatile in steam; yield 18 g. The nitro-compound (16 g.) was reduced to 5-chloro-6-amino-ψ-cumene with tin (20 g.) and concentrated hydrochloric acid (50 c.c.), and the product isolated by making the reaction liquid alkaline with caustic soda, followed by distillation in steam. 5-Chloro-6-amino-ψ-cumene forms white crystals, m. p. 51°, readily volatile in steam. By the method used above for 5-chloro-*o*-tolylthiocarbimide, it was converted into 5-chloro-ψ-cumene-6-thiocarbimide, white crystals, m. p. 36°; this is not readily volatile with steam but may be purified by recrystallisation from light petroleum.

α-(5-*Chloro*-6-ψ-*cumyl*)-β-(β-*naphthyl*)*thiocarbamide*, minute, colourless crystals, m. p. 161°, from dilute alcohol (Found : S, 9·1. $C_{20}H_{19}N_2SCl$ requires S, 9·03%).

3-*Chloro*-p-*anisylthiocarbimide*. 4-Nitro-*o*-anisidine was diazotised and treated with cuprous chloride, giving 2-chloro-*p*-nitroanisole, pale yellow silky needles, m. p. 96°. The nitro-compound (20 g.) was reduced with tin (60 g.) and concentrated hydrochloric acid (150 c.c.), and the amino-compound isolated by making the reaction liquid alkaline and distilling it with steam. 3-Chloro-*p*-anisidine forms white glistening plates, m. p. 65°. The amine (10 g.) was converted into 3-chloro-*p*-anisylthiocarbimide by dissolving it in 2*N*-hydrochloric acid (400 c.c.) and shaking the solution with thiocarbonyl chloride (15 g.) for 24 hours. The resulting pale yellow solid was filtered off, washed with water, and recrystallised from acetone, separating in beautiful, white, silky needles, m. p. 89°.

α-(3-*Chloro*-p-*anisyl*)-β-(α-*naphthyl*)*thiocarbamide*, prepared by heating equimolecular proportions of the foregoing thiocarbimide and α-naphthylamine in benzene solution under reflux, was recrystallised from alcohol, and formed colourless, felted needles, m. p. 174° (Found: S, 9·4. $C_{18}H_{15}ON_2SCl$ requires S, 9·3%).

4-Chloro-*m*-anisylthiocarbimide, prepared from 5-nitro-*o*-anisidine by a process exactly analogous to that described under 3-chloro-*p*-anisylthiocarbimide, formed white crystals, m. p. 51°, readily soluble in acetone. α-(4-*Chloro*-m-*anisyl*)-β-(α-*naphthyl*)*thiocarbamide*, separated as minute, colourless needles from dilute alcohol, m. p. 155° (Found: S, 9·4. $C_{18}H_{15}ON_2SCl$ requires S, 9·3%).

5-*Chloro*-o-*anisylthiocarbimide*, $CH_3O{\cdot}C_6H_3Cl{\cdot}NCS$ (2 : 5 : 1). 4-Chloro-*o*-anisidine (19 g.) was dissolved in carbon tetrachloride (200 c.c.), and the solution gradually added to thiocarbonyl chloride (15 g.) suspended by vigorous stirring in water (300 c.c.). Stirring was continued for 2 hours, after which the carbon tetrachloride layer was removed, the solvent evaporated on the water-bath, and the thiocarbimide purified by distillation in steam; white crystals, m. p. 61°.

5-*Chloro*-o-*anisylthiocarbamide* forms colourless glistening needles, m. p. 133° (Found: S, 14·6. $C_8H_9ON_2SCl$ requires S, 14·8%).

5-*Chloro*-m-*anisylthiocarbimide*. *s*-Trinitrobenzene was converted by treatment with sodium methoxide into *s*-dinitroanisole. The latter was reduced with alcoholic ammonium sulphide to *s*-nitroanisidine, orange-yellow needles, m. p. 121°. This compound was converted into *s*-chloronitroanisole by diazotisation and treatment with an acid solution of cuprous chloride. The chloronitro-compound, almost white plates, m. p. 100°, was reduced with tin and hydrochloric acid to 5-chloro-*m*-anisidine, which formed small white crystals, m. p. 27°. By treatment with thiocarbonyl chloride in the manner already described, this was converted into 5-chloro-*m*-anisylthiocarbimide, colourless crystalline plates, m. p. 36°.

α-(5-*Chloro*-m-*anisyl*)-β-(p-*tolyl*)*thiocarbamide* formed colourless, silky needles, m. p. 136° (Found : S, 10·44. $C_{15}H_{15}ON_2SCl$ requires S, 10·4%).

3 : 4-, 2 : 6-, and 2 : 5-Dimethoxyphenylthiocarbimides were prepared by the method already described (Dyson, George, and Hunter, J., 1927, 441).

3 : 5-*Dimethoxyphenylthiocarbimide.* Considerable difficulty was encountered in the preparation of this compound. Finally, it was obtained from the *s*-nitroanisidine (mentioned above) by diazotisation in sulphuric acid solution and warming on the water-bath : the diazonium group was replaced by hydroxyl, giving the *s*-nitroresorcinol monomethyl ether (yellow plates, m. p. 143°). Treated with methyl sulphate and anhydrous potassium carbonate in xylene suspension, this compound gave a good yield of dimethoxynitrobenzene, long, pale yellow needles, m. p. 90°, which on reduction with tin and hydrochloric acid gave 3 : 5-dimethoxyaniline, white crystals, m. p. 60°. When this amine was treated with thiocarbonyl chloride in the manner described by Dyson, George, and Hunter (*ibid.*), it yielded 3 : 5-dimethoxyphenylthiocarbimide, colourless plates, m. p. 51°.

α-3 : 5-*Dimethoxyphenyl*-β-p-*tolylthiocarbamide* forms glistening white plates, m. p. 148° (Found S, 10·6. $C_{16}H_{18}O_2N_2S$ requires S, 10·6%).

Benzaldehyde-4-*thiocarbimide.* 4-Aminobenzaldehyde (14 g.) was finely powdered and dissolved in 10% hydrochloric acid (1500 c.c.). The solution, filtered from a small amount of insoluble matter, was shaken with thiocarbonyl chloride (15 g.) for 10 hours. The resulting brownish precipitate was filtered off, dried, and extracted with light petroleum. The filtered extract was allowed to evaporate spontaneously, and *benzaldehyde*-4-*thiocarbimide* separated in beautiful golden plates, m. p. 71°; it had an odour strongly resembling that of piperonal (Found : S, 19·6. C_8H_5ONS requires S, 19·7%).

Benzaldehyde-3-*thiocarbimide*, prepared in exactly the same way, crystallised in white needles from light petroleum, m. p. 42° (Found : S, 19·6. C_8H_5ONS requires S, 19·7%).

Diphenyl-4-*thiocarbimide* (*xenylthiocarbimide*). 4-Aminodiphenyl (xenylamine) (6 g.) was dissolved in chloroform (100 c.c.; the amine is not very soluble), and the solution added to thiocarbonyl chloride (7 g.) suspended in water (300 c.c.). After 3 hours' stirring, the chloroform layer was withdrawn, the solvent evaporated on the water-bath, and the residue distilled in steam. The thiocarbimide was only slowly volatile, requiring several days for complete distillation. Superheated steam decomposes the compound. It forms long glistening plates, m. p. 64°.

During the course of this work, a number of derivatives of thiourethane (thioncarbonic ethyl ester) have been prepared of the general formula R·NH·CS·OEt. The characteristics of these compounds are recorded in Table VIII.

TABLE VIII.

R in the formula R·NH·CS·O·C_2H_5.	M. p.	General appearance.
2-Nitrophenyl	59°	Lemon-yellow needles.
3-Nitrophenyl	115	Pale yellow needles.
4-Nitrophenyl	175	Colourless silky needles.
2-Nitro-3-methylphenyl	110	Pale yellow needles.
2-Nitro-4-methylphenyl	72	Orange-yellow needles.
2-Nitro-6-methylphenyl	109	Pale yellow needles.
3-Nitro-4-methylphenyl	89	Colourless felted needles.
3-Nitro-6-methylphenyl	112	Colourless needles.
4-Nitro-2-methylphenyl	116	Colourless felted needles.
4-Nitro-2-anisyl	76	Small yellow needles.
3-Nitro-4-fluorophenyl	118	Golden-yellow needles.
3-Chlorophenyl	82	Colourless needles.
4-Chlorophenyl	105	Long colourless needles.
2 : 4-Dichlorophenyl	79	Large colourless plates.
2 : 5-Dichlorophenyl	80	Colourless glistening plates.
3 : 5-Dichlorophenyl	131	Colourless silky needles.
3-Fluorophenyl	84	Colourless needles.
4-Fluorophenyl	86	Long colourless needles.
3-Bromophenyl	94	Long glistening needles.
4-Bromophenyl	107	Colourless needles.
3-Iodophenyl	107	Small colourless needles.
4-Iodophenyl	98	Long colourless needles.
3-Tolyl	67	Colourless plates.
4-Tolyl	85	Colourless prisms.
2 : 3-Dimethylphenyl	108	Colourless needles.
2 : 5-Dimethylphenyl	85	Colourless glistening plates.
3 : 5-Dimethylphenyl	88	Large colourless plates.
2-Methoxyphenyl	65	Colourless shining plates.
3-Methoxyphenyl	85	Long colourless needles.
4-Methoxyphenyl	68	Glistening plates.
2 : 5-Dimethoxyphenyl	72	Thick colourless needles.
3 : 4-Dimethoxyphenyl	72	Colourless silky needles.
3 : 5-Dimethoxyphenyl	83	Colourless needles.
3-Ethoxyphenyl	75	Colourless shining needles.
4-Ethoxyphenyl	95	Thick colourless plates.
2-Chloro-3-methylphenyl	77	Small colourless plates.
2-Chloro-5-methylphenyl	59	Colourless shining needles.
3-Chloro-2-methylphenyl	88	Colourless needles.
3-Chloro-4-methylphenyl	88	Colourless shining needles.
3-Chloro-5-methylphenyl	105	Minute colourless prisms.
3-Chloro-6-methylphenyl	81	Colourless glistening plates.
4-Chloro-2-methylphenyl	79	Small shining plates.
4-Chloro-3-methylphenyl	101	Colourless silky needles.
3-Chloro-4 : 6-dimethylphenyl	115	Colourless shining needles.
3-Chloro-4-methoxyphenyl	96	Colourless glistening needles.
3-Chloro-5-methoxyphenyl	86	Long shining needles.
3-Chloro-6-methoxyphenyl	81	Colourless silky needles.
4-Chloro-3-methoxyphenyl	124	Minute colourless prisms.
3-Cyanophenyl	95	Colourless shining plates.
4-Cyanophenyl	110	Colourless glistening needles.
3-Aldehydophenyl	147	Pale yellow shining needles.
4-Aldehydophenyl	135	Golden needles.
4-Acetylphenyl	111	Colourless silky needles.
Diphenyl-4	117	Short colourless needles.

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