60. *Thiocyanogen Chloride. Part III.*[1] *Preparation of Solutions in Acetic Acid and Their Application in the Thiocyanation of Aryl Ethers and Anilides.*

By R. G. R. Bacon and R. G. Guy.

Reactions between metal thiocyanates and halogens are discussed. A rapid reaction in acetic acid between lead thiocyanate (1 mol.) and chlorine (2 mol.) gives a solution of thiocyanogen chloride, which is converted into thiocyanogen if more lead thiocyanate is added. Thiocyanogen chloride solutions were also obtained from potassium thiocyanate and chlorine in acetic acid, and from lead thiocyanate and phenyl iododichloride, but not from thiocyanates and dichloramine T. Aryl ethers and anilides, which are unreactive towards thiocyanogen, give thiocyanato-derivatives in high yield when treated with thiocyanogen chloride in acetic acid: $\mathrm{PhX + Cl{\cdot}SCN \longrightarrow}$ $p\text{-}\mathrm{C_6H_4X{\cdot}SCN + HCl}$. These nuclear aromatic thiocyanations resemble corresponding substitutions by molecular halogen in that the rate of reaction is affected by the polarity of the solvent and by the nature of the substituent X: rate for (X =)$\mathrm{NMe_2 > OH > OMe > NHBz > NHAc > OPh > NMeAc}$. Available rate data suggest a total reaction order of 2.

A PROCEDURE previously reported[1,2] for obtaining a solution of thiocyanogen chloride consists in preparing thiocyanogen solution from a metal thiocyanate by a conventional method and treating it with one molecular proportion of chlorine:

$$\mathrm{(SCN)_2 + Cl_2 \longrightarrow 2Cl{\cdot}SCN} \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (1)$$

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[1] Part II, Bacon and Irwin, *J.*, 1958, 778.
[2] Angus and Bacon, *J.*, 1958, 774.

We have since examined some variations on this procedure and particularly the production of thiocyanogen chloride solutions from lead thiocyanate and chlorine in one operation.

Little has been added to knowledge of reactions between metal thiocyanates and halogens since Söderbäck's investigations.[3] He examined many examples of the reaction: $2MSCN + Hal_2$ (solution) $\longrightarrow$ $2MHal + (SCN)_2$ (solution). He reported that bromine reacted with several thiocyanates, the ease of reaction being influenced by the nature of the metal and possibly by the dryness of the solvent; that chlorine (studied only in carbon tetrachloride) reacted with silver or mercuric thiocyanate but not with the lead salt; that reaction with iodine was confined to silver and mercuric thiocyanate and was reversible. Treatment of a suspension of excess of lead thiocyanate with bromine in a suitable solvent has subsequently been the customary method for preparing thiocyanogen solutions.[4]

We were particularly interested in using thiocyanogen chloride in acetic acid. It was expected that this solvent, as in the case of nuclear aromatic halogenation, would be a better medium for nuclear aromatic thiocyanation than the carbon tetrachloride which we had previously used.[2] A suspension of excess of lead thiocyanate was found to react rapidly with chlorine in acetic acid to give thiocyanogen:

$$Pb(SCN)_2 + Cl_2 \longrightarrow PbCl_2 + (SCN)_2 \qquad (2)$$

When however the reagents were used exactly in the ratio required by equation (3), a solution of thiocyanogen chloride resulted:

$$Pb(SCN)_2 + 2Cl_2 \longrightarrow PbCl_2 + 2Cl{\cdot}SCN \qquad (3)$$

This reaction is written more simply as:

$$-Pb-SCN + Cl_2 \longrightarrow -Pb-Cl + Cl{\cdot}SCN \qquad (3a)$$

If more lead thiocyanate was added to the solution of thiocyanogen chloride, the latter was converted into thiocyanogen:

$$Pb(SCN)_2 + 2Cl{\cdot}SCN \longrightarrow PbCl_2 + 2(SCN)_2 \qquad (4)$$

Again, this reaction is written more simply as:

$$-Pb-SCN + Cl{\cdot}SCN \longrightarrow -Pb-Cl + (SCN)_2 \qquad (4a)$$

To ascertain whether reaction (3) occurred quantitatively, the loss in weight of the lead salt was accurately measured after the mixture had been stirred for a few minutes at room temperature. In acetic acid there was exact agreement with the theoretical figure. The resulting solution exhibited the expected properties [1,2] of thiocyanogen chloride; *e.g.*, it instantly converted cyclohexene into 2-chlorocyclohexyl thiocyanate. The account given below, and data to be presented in later papers, show that solutions thus prepared are suitable for nuclear thiocyanation of numerous aromatic compounds which are unaffected by thiocyanogen. The products have usually been obtained in good yield and have consistently proved to be thiocyanates and not chlorides. The nature of the solvent affects the ease with which reaction (3) occurs. For example, whereas it was quantitative in acetic acid, under similar conditions of time and temperature (15 min.; 20°) it occurred to the extent of 93% in chloroform and 35% in carbon tetrachloride; for the last solvent Söderbäck [3] reported no reaction.

Reaction (4) was demonstrated by experiments of the kind illustrated in Fig. 1. The first section of the curve shows the slow decline in concentration of a thiocyanogen chloride solution ($\sim$0·05M), as measured iodometrically, which is observed at room temperature. Addition (*A*) of cyclohexene ($<$1 mol.) immediately removes some of the thiocyanogen chloride. Subsequent addition (*B*) of lead thiocyanate converts the rest of the reagent into thiocyanogen. The latter does not react when more cyclohexene is added (*C*), but it immediately reacts [2] when dimethylaniline is added (*D*), giving *NN*-dimethyl-*p*-thiocyanatoaniline.

[3] Söderbäck, *Annalen*, 1919, **419**, 217.

[4] Wood, " Organic Reactions," Wiley and Sons, New York, 1946, Vol. III, p. 240.

The production of thiocyanogen chloride may be attributed to reactions (2) and (1) occurring consecutively or to the single bimolecular reaction (3*a*). According to the latter view, thiocyanogen chloride is an intermediate in preparations of thiocyanogen from excess of thiocyanate and chlorine, when reaction (4*a*) follows (3*a*). The relative proportions of thiocyanate and chlorine determine the product, since, if local concentrations of thiocyanate give thiocyanogen, its chloride will be re-formed by reaction (1) as long as chlorine is also present in the solution. When thiocyanogen is prepared from a thiocyanate and bromine, there may likewise be intermediate formation of thiocyanogen bromide, Br•SCN, but the very ready dissociation of this compound complicates the situation. For bromine, the reaction corresponding with equation (1) is an equilibrium,[1] quantitative aspects of which have recently been examined with the aid of infrared spectroscopy by our colleagues Dr. A. D. E. Pullin and Mrs. M. J. Nelson.[5] The difficulty of demonstrating the existence of thiocyanogen bromide at ordinary temperatures by chemical tests is presumably due to the greater reactivity of the bromine with which it is in equilibrium. The reactions of iodine bromide, which, unlike thiocyanogen bromide, can be handled in the solid state at room temperature, are likewise complicated by its dissociation in organic solvents.[6]

FIG. 1. *Reactions of* Cl·SCN.

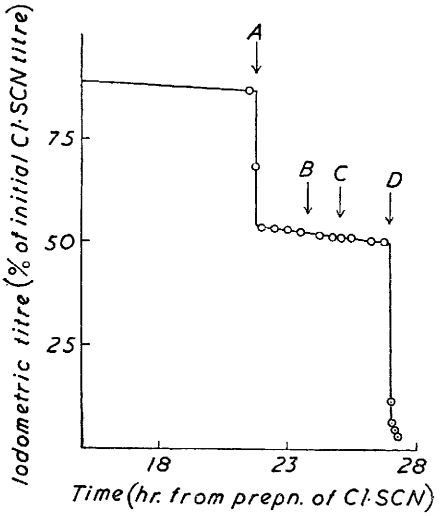
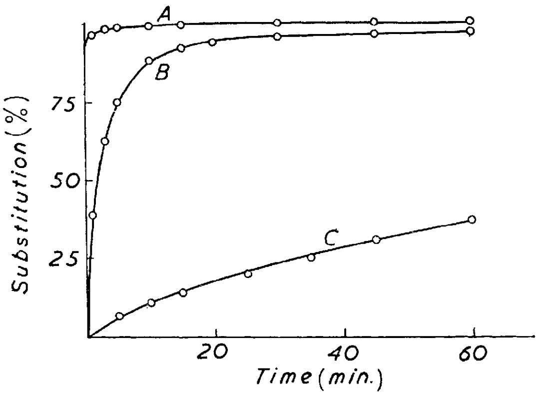


FIG. 2. *Reaction of 2-methoxynaphthalene with* Cl·SCN (0·1N., 2 *mol.*), *at* 20° *in darkness, in acetic acid* (*A*), *chloroform* (*B*), *and carbon tetrachloride* (*C*).



Successive bimolecular steps, such as (3*a*) and (4*a*), may be general for reactions of halides (or pseudohalides) with halogens (or pseudohalogens). There is kinetic evidence for this in reactions of hydrogen iodide with chlorine and with cyanogen halides.[7] For some pairs of reagents, reaction ceases or becomes difficult after the first step. Thus, metal cyanides and halogens give cyanogen halides rather than cyanogen.[8] Similarly, metal cyanates and halogens give dimeric or trimeric forms of OCN•Hal[9] and solutions of the compound $(OCN)_2$ appear to be either unobtainable or obtainable only with great difficulty.[10]

Assuming that the solubility of heavy-metal thiocyanates in organic solvents is too

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[5] Nelson and Pullin, *J.*, in the press.
[6] Bennett and Sharpe, *J.*, 1950, 1383; Sharpe, *J.*, 1953, 3713.
[7] Mooney and Reid, *J.*, 1933, 1315.
[8] Williams, " Cyanogen Compounds," Arnold and Co., London, 1948.
[9] Birckenbach and Linhard, *Ber.*, 1929, **62**, 2261; 1930, **63**, 2528, 2544.
[10] Birckenbach and Kellermann, *Ber.*, 1925, **58**, 786; Hunt, *J. Amer. Chem. Soc.*, 1931, **53**, 2111; 1932, **54**, 907.

slight to be a significant factor, we envisage reactions (3*a*) and (4*a*) as heterogeneous, involving solvent-influenced attack of the halogen on the crystal surface, followed by disruption and penetration of the crystal lattice. Contemporary investigations with thiocyanates show that the metal–thiocyanate bond may vary in character. No information appears to be available concerning the bonds in lead thiocyanate, but Lindqvist[11] has reported an examination, by *X*-ray crystallography, of silver thiocyanate, which Söderbäck used in some of his experiments.[3] For this salt the lattice consists of zig-zag chains, in which silver atoms are linked through covalent bonds to the sulphur atom of one thiocyanate group and also to the nitrogen atom of the next.

The following variations on the preparation of thiocyanogen chloride by reaction (3) were briefly examined, mainly for their theoretical interest:

(*a*) Potassium thiocyanate and chlorine in equimolecular proportions rapidly reacted in acetic acid: $KSCN + Cl_2 \longrightarrow KCl + Cl{\cdot}SCN$. The resulting solution of thiocyanogen chloride gave a good yield of 2-chlorocyclohexyl thiocyanate with cyclohexene. Potassium thiocyanate is substantially soluble in acetic acid. Its hygroscopicity is a disadvantage, since water decomposes both thiocyanogen and its chloride.

(*b*) Phenyl iododichloride contains labile chlorine and it has been used as an alternative to bromine in preparing thiocyanogen from lead thiocyanate.[12] When these reagents were mixed in chloroform, in the proportions shown by equation (5), the product proved to be thiocyanogen chloride:

$$2PhICl_2 + Pb(SCN)_2 \longrightarrow 2PhI + PbCl_2 + 2Cl{\cdot}SCN \quad . \; . \; . \; . \; . \; . \quad (5)$$

Solutions thus obtained were employed in preparations of 2-chlorocyclohexyl thiocyanate and *p*-thiocyanatoacetanilide. Phenyl iododichloride offers no practical advantage over chlorine. It gives thiocyanogen chloride with thiocyanogen also, though the reaction appears to be more difficult than its reaction with lead thiocyanate: $PhICl_2 + (SCN)_2 \longrightarrow PhI + 2Cl{\cdot}SCN$.

(*c*) Dichloramine T likewise contains labile chlorine, and was examined with sodium iodide; in acetic acid it acts as a source of iodine chloride:[13] $p\text{-}C_6H_4Me{\cdot}SO_2{\cdot}NCl_2 + 2NaI + 2AcOH \longrightarrow p\text{-}C_6H_4Me{\cdot}SO_2{\cdot}NH_2 + 2NaOAc + 2ICl$. We found no evidence for an analogous reaction with potassium, ammonium, or lead thiocyanates.

Nuclear Aromatic Thiocyanation with Thiocyanogen Chloride.—The thiocyanation of mononuclear aromatic compounds with thiocyanogen is normally restricted to amines and phenols,[4] though it may be applied even to benzene[14] if carried out in the presence of Friedel–Crafts catalysts, which presumably act by polarising the S–S bond of thiocyanogen. Similarly, the polar character of the S–Cl bond in thiocyanogen chloride makes this a more powerful reagent than thiocyanogen for such electrophilic substitutions.[15] As with halogenations, the rate of these thiocyanations is affected by the polarity of the solvent. This is illustrated in Fig. 2 for the thiocyanation of 2-methoxynaphthalene. The presence of the naphthalene nucleus makes this a more reactive aryl ether than anisole and it is slowly substituted even by thiocyanogen (92% in 10 days in ether).[16] Its reaction with thiocyanogen chloride at 20° was too fast for measurement in acetic acid, was fast in chloroform, and required about 20 hr. for completion in carbon tetrachloride. A practically quantitative yield of 2-methoxy-1-thiocyanatonaphthalene was obtained in all cases.

For thiocyanations in acetic acid we have used $\sim$0·3N-Cl·SCN, usually at 20°, and occasionally at 40°. The reactions have been followed by iodometric titration, but this does not give a highly accurate measure of the rate of thiocyanation because the decomposition of thiocyanogen chloride (probably involving polymerisation) contributes, to a minor

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[11] Lindqvist, *Acta Cryst.*, 1957, **10**, 29.
[12] Neu, *Ber.*, 1939, **72**, 1505.
[13] Bradfield, Orton, and Roberts, *J.*, 1928, 782.
[14] Söderbäck, *Acta Chem. Scand.*, 1954, **8**, 1851.
[15] Angus, Bacon, and Guy, *Chem. and Ind.*, 1955, 564.
[16] Kaufmann and Liepe, *Ber. deut. pharm. Ges.*, 1923, **33**, 139.

degree, to the fall in titre. In the absence of other compounds, the rate of decomposition of thiocyanogen chloride in acetic acid solution at 20° is of the order of 0·5—1% per hr. If this spontaneous decomposition accompanies aromatic thiocyanation, and if the aromatic product can be isolated more or less quantitatively, then comparison of yield with titre should reveal the extent of spontaneous decomposition. The typical data shown in the Table indicate a rate of 0·5—3% per hr. for decomposition of the reagent and thus suggest that the process is not greatly affected by the simultaneous substitution. This small correction has been applied in drawing thiocyanation curves (Fig. 2 and 3); it has been assumed that decomposition is linear with respect to time. Our usual procedure in preparative work was to employ the reagent in 100% excess and to follow the course of the reaction by titration of aliquot parts.

FIG. 3. *Reaction of* PhOMe (*A*), Ph·NHBz (*B*), Ph·NHAc (*C*), *and* PhOPh (*D*) *with* Cl·SCN (0·3N, 2 *mol.*) *in acetic acid at* 20° *in darkness.*

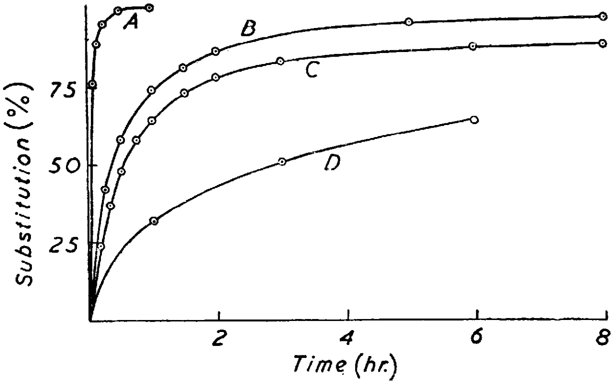

Fig. 3 and the data in the Table illustrate the thiocyanation of ethers and anilides. The products were obtained in good yield and required little purification. Anisole, diphenyl ether, and acetanilide gave the *para*-thiocyanates, which were known from other methods of preparation. The product from benzanilide was likewise the *para*-derivative, since it could also be made by benzoylation of *p*-thiocyanatoaniline. No chloro-derivatives were detected. *N*-Methylacetanilide failed to react under the conditions examined. These results, together with earlier observations,[2] give the following order of reactivity of PhX in the thiocyanation, PhX + Cl·SCN $\longrightarrow$ p-C_6H_4X·SCN + HCl: (X =)NMe_2 > OH > OMe > NHBz > NHAc > OPh > NMeAc. This is identical with the order of

Preparation of aromatic thiocyanates, with thiocyanogen chloride in acetic acid (500 *ml.*) *at* 20°.

Aryl ether or anilide	(10⁻² mole)	Cl·SCN (10⁻² mole)	Approx. time for 50% thiocyanation (hr.) [a]	Duration of prepn. (hr.)	Thiocyanate isolated (10⁻² mole)	Total Cl·SCN consumed [b] (10⁻² mole)
2-$C_{10}H_7$·OMe ...	4·00	8·00	<0·05 [c]	1	4·00 (100%)	4·24
PhOMe	,,	4·00	0·1	8	3·28 (82%)	3·48
,, ...	,,	8·00	0·05	1	4·00 (100%) [d]	4·24
PhOPh	,,	,,	3	24	3·60 (90%)	4·88
,, ...	,,	,,		10 (at 40°)	3·76 (94%)	5·84
Ph·NHBz	,,	,,	0·3	8	3·84 (96%)	4·24
Ph·NHAc	,,	4·00	3	27	2·60 (65%)	3·36
,, ...	,,	8·00	0·5	8	3·52 (88%)	4·08
,, ...	2·62	5·24		18 (in $CHCl_3$) [e]	1·83 (70%)	4·77
Ph·NMeAc	4·00	8·00	—	168	Nil	4·88

[a] From rate curves (Fig. 3). [b] By iodometric titration at the end of the preparation. [c] See also Fig. 2. [d] Yield based on titration data in this case, since the compound was too soluble for quantitative isolation under the conditions used. [e] Comparative experiment with Cl·SCN prepared from $PhICl_2$ in $CHCl_3$.

reactivities of these benzene derivatives in nuclear substitutions by molecular halogen in acetic acid.[17]

An indication of the kinetics of the thiocyanations was obtained by applying a "fractional life" formula[18] to some of the data. For acetanilide and thiocyanogen chloride, in darkness in acetic acid at 20°, this gave values of 2·1—2·2 (at 30—60% reaction) for the total reaction order. For 2-methoxynaphthalene the values were 1·8—2·3 (at 40—80% reaction) in chloroform and 1·7—1·9 (at 20—60% reaction) in carbon tetrachloride. These results suggest a total reaction order of 2. Reaction is presumed to involve electrophilic substitution by $\overset{\delta-}{\mathrm{Cl}}\text{–}\overset{\delta+}{\mathrm{SCN}}$. This appears to be a simpler process than the corresponding iodination by iodine chloride, which, with acetanilide or anisole, shows a total reaction order of 3 and is accompanied by some chlorination.[19] The thiocyanation of aromatic hydrocarbons by thiocyanogen chloride shows special features which will be discussed in later papers.

EXPERIMENTAL

Preparation of Thiocyanogen Chloride from Lead Thiocyanate in Acetic Acid.—"AnalaR" acetic acid was dried by refluxing it for 4 hr. with 5% of acetic anhydride; the dried acid was used without removal of the anhydride for all the experiments described in this paper. Dry chlorine was passed into this solvent to give a ~0·3N(~0·15M)-solution, 500 ml. of which were placed in the reaction flask and analysed by addition of aliquot parts to 10% methanolic potassium iodide (~200% excess), followed by iodometric titration with 0·1N-thiosulphate. Lead thiocyanate was prepared by precipitation from "AnalaR" lead nitrate and "AnalaR" ammonium thiocyanate and was recrystallised from water, dried in a vacuum, ground, and stored in a dark bottle.[20] Lead thiocyanate was added to the chlorine solution in the exact ratio, $\mathrm{Pb(SCN)_2}$ 1 mol. : $\mathrm{Cl_2}$ 2 mol., and the mixture was stirred for 15 min. at 20°. The green-yellow colour due to the chlorine was replaced by the orange-yellow of thiocyanogen chloride and there was a slight rise in temperature (3—5°) during the first 2—3 min.

After 15 minutes' stirring, the iodometric titre of the resulting thiocyanogen chloride was consistently about 97% of that of the chlorine solution. The following results illustrate subsequent rates of decomposition of the reagent, as assessed by iodometric titration:

Time, from end of stirring (hr.)	0·5	1	2	4	11	24	50
Initially 0·331N-Cl·SCN, kept in dark at 20° (decomp. %)	1	3	7	9	11	12	
Initially 0·325N-Cl·SCN, kept in dark at 40° (decomp. %)	4	5	7	9	15	31	78 *
Initially 0·346N-Cl·SCN, under ultraviolet irradiation † at ~48° (decomp. %)	7	13	19	30			

* Orange amorphous precipitate now present. † 250 watt "Mazda" ME/D mercury-vapour lamp.

The reaction between lead thiocyanate and chlorine in organic solvents was examined by stirring the mixture for 15 min. in darkness at 20°, filtering off the lead salt, and determining its change in weight. The following are typical results:

Solvent	AcOH	$\mathrm{CHCl_3}$ [a]	$\mathrm{CCl_4}$
Chlorine concentration	0·3501N	0·3161N	0·3542N
$\mathrm{Pb(SCN)_2}$ added (g. per 480 ml. of solution)	13·588	12·270	13·746
Pb salts isolated (g.)	11·680 [b]	10·664 [c]	13·077 [c]
Theor. wt. of isolated salt for complete conversion into $\mathrm{PbCl_2}$ (g.)	11·686	10·552	11·820
Calc. conversion (%)	100·3	93·5	34·7

[a] Ethanol-free. [b] Gave no thiocyanate reaction with aqueous $\mathrm{FeCl_3}$. [c] Gave strong thiocyanate reaction.

Preparation of Thiocyanogen Chloride from Potassium Thiocyanate in Acetic Acid.—Finely ground "AnalaR" potassium thiocyanate was dried over phosphoric oxide for 1 week in a vacuum and was added to 500 ml. of 0·4N-chlorine in dry acetic acid, in 1 : 1 molecular ratio, and the mixture was stirred for 15 min. at 20°. An exothermic reaction was apparent (4° rise)

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[17] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.

[18] Frost and Pearson, "Kinetics and Mechanism," Wiley and Sons, New York, 1953, p. 42.

[19] Lambourne and Robertson, *J.*, 1947, 1167.

[20] Lambou and Dollear, *Oil and Soap*, 1946, **23**, 97.

during the first 3 min. The titre of the resulting thiocyanogen chloride solution was 94% of that of the chlorine solution. Addition of cyclohexene (1 mol.) resulted in a rapid reaction, giving 1-chloro-2-thiocyanatocyclohexane (78%), b. p. 152—153°/20 mm., n_D^{25} 1·5250, after redistillation.

Preparation of Thiocyanogen Chloride with Phenyl Iododichloride.—(*a*) 500 ml. of a chloroform solution of freshly prepared phenyl iododichloride[21] (0·25N; checked by iodometric titration) were stirred for 30 min. at 24° with the calculated quantity of lead thiocyanate (1 mol. per 2 mol. of $PhICl_2$). The titre of the resulting thiocyanogen chloride solution was 89% of that of the phenyl iododichloride solution. It reacted rapidly with cyclohexene (1 mol.) at room temperature and the solution gave, on fractional distillation, iodobenzene and 1-chloro-2-thiocyanatocyclohexane (47%), b. p. 77—79°/0·03 mm., n_D^{25} 1·5267, but no dichlorocyclohexane fraction. A solution of thiocyanogen chloride similarly prepared gave a 70% yield of 4-thiocyanatoacetanilide (see Table).

(*b*) 0·1114N-Thiocyanogen in chloroform was prepared from lead thiocyanate and bromine and was treated with phenyl iododichloride (1 mol.) at 0°. There was no change in titre on mixing and after 90 min. the titre was lower by 2·7%. After 2 hr. acetanilide was added, the reagent (reckoned as Cl·SCN) being in 100% excess. Iodometric titration indicated that 49% of the reagent had disappeared after 20 hr. at 0°, but the yield of 4-thiocyanatoacetanilide was only 10% after chromatographic separation from unchanged acetanilide (75% recovery). Thiocyanogen in carbon tetrachloride had no apparent effect at 0° on phenyl iododichloride, which is virtually insoluble in this solvent.

Thiocyanation of Ethers and Anilides.—Typical preparations were carried out under conditions summarised in the Table. The purified ether or anilide was added to the flask containing 500 ml. of ~0·3N(~0·15M)-thiocyanogen chloride in acetic acid, prepared as described above, and the mixture was gently stirred at constant temperature with the lead chloride still present. The disappearance of thiocyanogen chloride was followed by iodometric titration of aliquot parts. There appeared to be no significant difference between reactions carried out in daylight or darkness.

The thiocyanates were isolated as crystalline precipitates by filtering off the lead chloride, diluting the acetic acid solution with ice and water (3·5 l.), and keeping the mixture overnight at about 0°. The products were fairly pure; recrystallisation raised their m. p. by 1—3°. 1-Methoxy-4-thiocyanatobenzene was slightly soluble in cold dilute acetic acid, and the yield could be augmented by neutralising the filtrate from the main crop with ammonia and again chilling the solution.

1-Methoxy-4-thiocyanatobenzene crystallised from ethanol in needles, m. p. 33—34°, in agreement with the literature[22] (Found: C, 58·0; H, 4·4; N, 8·2; S, 19·15. Calc. for C_8H_7ONS: C, 58·2; H, 4·3; N, 8·5; S, 19·4%). 2-Methoxy-1-thiocyanatonaphthalene crystallised from ethanol in cream-coloured prisms, m. p. 132—134°; Kaufmann and Liepe[16] give 134° (Found: C, 66·6; H, 4·25; N, 6·2; S, 15·25. Calc. for $C_{12}H_9ONS$: C, 66·95; H, 4·2; N, 6·5; S, 14·9%). 1-Phenoxy-4-thiocyanatobenzene distilled at 144—146°/0·1 mm. and crystallised from light petroleum in prisms, m. p. 49—50°; Hester and Craig[23] give 45—48° (Found: C, 69·1; H, 3·7; N, 6·25; S, 14·05. Calc. for $C_{13}H_9ONS$: C, 68·7; H, 4·0; N, 6·15; S, 14·1%). 4-Thiocyanatoacetanilide crystallised from ethanol in needles, m. p. 189—190°; Dienske[24] gives 189° (Found: C, 55·9; H, 4·15; N, 14·5; S, 16·85. Calc. for $C_9H_8ON_2S$: C, 56·25; H, 4·2; N, 14·6; S, 16·7%). 4-*Thiocyanatobenzanilide* crystallised from ethanol in leaflets, m. p. 158—160° (Found: C, 66·2; H, 3·9; N, 10·85; S, 12·6. $C_{14}H_{10}ON_2S$ requires C, 66·15; H, 3·95; N, 11·0; S, 12·6%). It was also prepared by thiocyanating aniline by a procedure described for dimethylaniline[25] and treating the resulting 4-thiocyanatoaniline (82% yield), in cooled pyridine solution, with benzoyl chloride; the m. p. was 160—161°, not depressed by the sample made from benzanilide.

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[21] *Org. Synth.*, Coll. Vol. III, p. 482.
[22] Riemschneider, Wojan, and Orlick, *J. Amer. Chem. Soc.*, 1951, **73**, 5905.
[23] Hester and Craig, U.S.P. 2,281,692.
[24] Dienske, *Rec. Trav. chim.*, 1927, **46**, 154.
[25] *Org. Synth.*, Coll. Vol. II, p. 574.