

470. *Thiocyanogen Chloride. Part IV.<sup>1</sup> Reaction with Aromatic Hydrocarbons; Heterolytic and Homolytic Substitution in Benzene Homologues.*

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In an organic solvent and with no added catalyst, thiocyanogen chloride effects nuclear thiocyanation in a much wider range of aromatic hydrocarbons than does thiocyanogen. Reactions between thiocyanogen chloride and *m*-xylene, higher benzene homologues, naphthalene, and anthracene are described. The relative rates of nuclear thiocyanation of the hydrocarbons are in the same order as their relative rates of nuclear substitution by molecular halogens. With ultraviolet irradiation, homolytic reaction occurs between thiocyanogen chloride and arylalkyl hydrocarbons, the result being replacement of an  $\alpha$ -hydrogen atom by the SCN group. This reaction is described for toluene, ethylbenzene, *m*-xylene, isopropylbenzene, diphenylmethane, and triphenylmethane; the three last-named hydrocarbons give an isothiocyanate instead of a thiocyanate. Polar effects in the hydrocarbon, assisted by a polar solvent, may successfully compete with the effect of light; *e.g.*, with irradiated solutions of thiocyanogen chloride in acetic acid, thiocyanation occurs partly in the nucleus of *m*-xylene and wholly in the nucleus of mesitylene.

THE nuclear thiocyanation of phenols, amines, and their derivatives by thiocyanogen chloride was described in earlier papers.<sup>1,2</sup> These reactions have similar characteristics to the heterolytic substitutions which an activated aromatic nucleus undergoes with molecular halogens or interhalogen compounds.<sup>3</sup> When aromatic hydrocarbons react with thiocyanogen chloride, two effects are possible, and these are likewise analogous to the results of halogenations of the hydrocarbons: nuclear thiocyanation may occur, by a presumed heterolytic mechanism; or side-chain thiocyanation may occur, by a homolytic mechanism, if the compound possesses an alkyl substituent containing at least one  $\alpha$ -hydrogen atom. The latter type of substitution provides the first example of a reaction involving homolysis of the Cl-S bond of thiocyanogen chloride.<sup>4</sup> Its easy occurrence was first noticed while we were examining the thiocyanation of 1-methylnaphthalene, details of which are given in Part V (following paper). The present paper concerns twelve other aromatic hydrocarbons, mainly homologues of benzene.

*Nuclear Thiocyanation.*—For halogens and interhalogen compounds, the known order of reactivity<sup>3</sup> towards an aromatic nucleus is:  $\text{Cl}_2 > \text{BrCl} > \text{Br}_2 > \text{ICl} > \text{I}_2$ . Thiocyanogen,  $(\text{SCN})_2$ , fits into this series between iodine chloride and iodine, while thiocyanogen chloride,  $\text{NCS-Cl}$ , occupies approximately the same position as iodine chloride. The rate curves shown in Fig. 1 illustrate nuclear substitution by some of these reagents in a fairly reactive hydrocarbon, 1-methylnaphthalene; 50% of monosubstitution was reached with both thiocyanogen chloride and iodine chloride in about 3 hr., and with bromine in about 1 min., while chlorine entered even more rapidly into disubstitution.

The only aromatic hydrocarbons known to undergo uncatalysed nuclear substitution by thiocyanogen are anthracene and some larger polycyclic compounds.<sup>5</sup> Söderbäck found that the reactivity of thiocyanogen is greatly enhanced by Friedel-Crafts catalysts, which lead to ready substitution even in benzene;<sup>6</sup> there seems to have been no

<sup>1</sup> Part III, Bacon and Guy, *J.*, 1960, 318.

<sup>2</sup> Angus and Bacon, *J.*, 1958, 774; Bacon and Irwin, *J.*, 1958, 778.

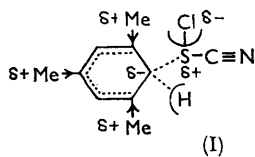
<sup>3</sup> de la Mare and Ridd, "Aromatic Substitution. Nitration and Halogenation," Butterworths, London, 1959.

<sup>4</sup> Bacon, Guy, Irwin, and Robinson, *Proc. Chem. Soc.*, 1959, 304.

<sup>5</sup> Wood and Fieser, *J. Amer. Chem. Soc.*, 1941, **63**, 2323.

<sup>6</sup> Söderbäck, *Acta Chem. Scand.*, 1954, **8**, 1851.

subsequent study of this method of thiocyanation. Without the aid of a catalyst, thiocyanogen chloride causes thiocyanation of a wider range of aromatic hydrocarbons than does thiocyanogen under similar conditions:  $\text{ArH} + \text{Cl}\cdot\text{SCN} \rightarrow \text{Ar}\cdot\text{SCN} + \text{HCl}$ . The greater reactivity of the chloride is attributed to polarisation of the Cl-S bond.<sup>2</sup> We have not yet explored the effect of catalysts on this reaction. By analogy with a mechanism postulated for aromatic substitutions effected by molecular halogens,<sup>3</sup> nuclear thiocyanation may be considered to involve heterolysis of a Cl-S bond, perhaps aided by associated molecules of solvent or catalyst, in a transition-state complex, such as that shown (I) for mesitylene and thiocyanogen chloride. Among hydrocarbons so far examined with the reagent, only anthracene (see below) has given evidence that chlorine may also enter the molecule.



Results of nuclear thiocyanation by thiocyanogen chloride are shown in Table 1 and Fig. 2.

FIG. 1. Reaction of 1-methylnaphthalene (1 mol.) in acetic acid in darkness at 20° with the reagents (2 mol.): 0.151M-Cl<sub>2</sub> (A), 0.167M-Br<sub>2</sub> (B), 0.161M-Cl·SCN (C), 0.158M-ICl (D).

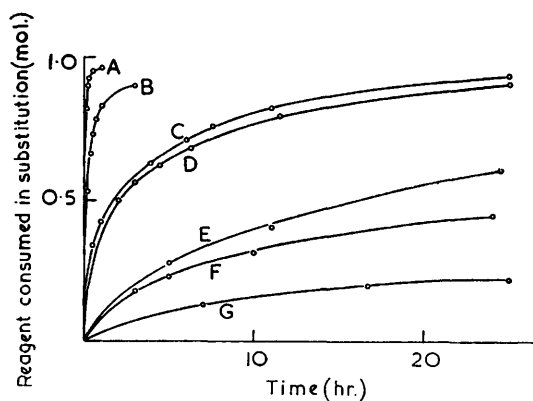
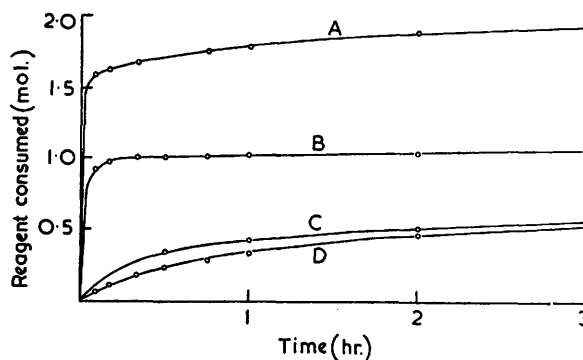


FIG. 2. Substitution of pentamethylbenzene (A), mesitylene (exp. i) (B), 1-methylnaphthalene (C), 2-methylnaphthalene (D), m-xylene (at 40°) (E), durene (F), and naphthalene (G) by Cl·SCN at 20° under the conditions given in Table 1.

Reactions were usually carried out in darkness because of the possible occurrence of some side-chain thiocyanation in daylight (cf. Part V). The solvent, acetic acid, is known to be a good medium for nuclear halogenations<sup>3</sup> and it had previously been found suitable for thiocyanation of anilides and phenolic ethers.<sup>1</sup> If a hydrocarbon fails to undergo substitution at 20–40°, success is unlikely at higher temperatures, since the spontaneous decomposition of the reagent will then be correspondingly rapid. Experiments (i), (ii), and (iii) with naphthalene illustrate the effect of temperature for a hydrocarbon of rather low reactivity towards thiocyanogen chloride. The reagent was customarily used in 100% excess, partly to increase the rate of substitution and partly to allow for some loss by spontaneous decomposition. Experiments (i), (ii), and (iii) with mesitylene illustrate the effect of varying the concentration of reagent. Its decomposition is usually very much slower than its reaction with a hydrocarbon, but an approximate allowance was made for

it, as previously described,<sup>1</sup> when rates of substitution were recorded. Reactions beyond the monothiocyanation stage were not observed.

In the monocyclic series of hydrocarbons, the presence of two or more methyl groups, *ortho* or *para* to the point of substitution, activates the nucleus sufficiently for reaction to occur with thiocyanogen chloride, while in the polycyclic series reactivity extends down to unsubstituted naphthalene. Relative reactivities are compared in Table I with those reported for bromination of the hydrocarbons by molecular bromine.<sup>3</sup> The close corre-

TABLE I. Reaction between hydrocarbons (1 mol.) and thiocyanogen chloride (2 mol.) in darkness in acetic acid (500 ml.).

Hydrocarbon	Cl:SCN (M)	Temp.	Time <sup>b</sup> for 50% substn. (hr.)	Relative rates <sup>c</sup> of bromination	Total time (hr.)	Total Cl:SCN consumed (mol.)	Yield of substn. product (mol.)
Toluene .....	0.150	40°	—	$6.05 \times 10^2$	72	1.66	Nil
<i>m</i> -Xylene .....	0.154	„	17	$5.14 \times 10^5$	24	1.46	0.60
Durene .....	0.156	20	32	$2.83 \times 10^6$	72	1.16	0.67
Mesitylene (i) .....	0.154	„	0.2	$1.89 \times 10^8$	3	1.08	0.90
(ii) <sup>a</sup> .....	0.098	„	0.3		6	1.08	0.91
(iii) <sup>a</sup> .....	0.049 <sup>a</sup>	„	4.0		20	0.81	0.56
Pentamethylbenzene...	0.154	„	<0.1	$8.1 \times 10^8$	1	1.06	0.96
Naphthalene (i) <sup>a</sup> .....	0.177	60	—	$1 \times 10^6$	11	1.96	0.20
(ii) <sup>a</sup> .....	0.183	40	~50		34	1.60	0.37
(iii) <sup>a</sup> .....	0.191	20	>120		117	1.16	0.42
2-Methylnaphthalene...	0.157	„	2.0		34	1.14	0.81
1-Methylnaphthalene...	0.161	„	1.7		25	1.12	0.92
Anthracene <sup>a</sup> .....	0.155 <sup>e</sup>	„	~0.1		5	1.10	0.76

<sup>a</sup> Reaction in daylight. <sup>b</sup> From rate curves (cf. Fig. 2). <sup>c</sup> Data from ref. 3, pp. 137, 173; they are for Br<sub>2</sub> in AcOH, relative to C<sub>6</sub>H<sub>6</sub> = 1. <sup>d</sup> 1 Mol. used. <sup>e</sup> 1.11 Mol. used.

spondence observed in the order of reactivity indicates that the thiocyanations and brominations respond similarly to the polar influences which operate in the aromatic hydrocarbons. A similar conclusion was reached for phenols, amines, and their derivatives.<sup>1</sup> The higher rate of catalysed thiocyanation is shown by the fact that with ~0.7M-solutions of thiocyanogen, and with aluminium chloride present, Söderbäck<sup>6</sup> observed complete consumption of the reagent within 0.5 hr., for both mesitylene and naphthalene (cf. Table I), at or below room temperature.

The product from thiocyanogen chloride and *m*-xylene was a liquid, shown to be 2,4-dimethyl-1-thiocyanatobenzene by an alternative preparation from diazotised 2,4-dimethylaniline. The identity of the products was shown by their physical constants and infrared absorption spectra, and by identification of the thiol obtained on reduction of the thiocyanate group<sup>7</sup> with lithium aluminium hydride. The product from mesitylene had the same m. p. as that described by Söderbäck<sup>6</sup> and was identical with a sample prepared from diazotised mesidine. The structures of the crystalline thiocyanates obtained from durene and pentamethylbenzene are unambiguous and alternative methods of preparation were not carried out. They showed the strong, sharp infrared absorption peak at 2160 cm.<sup>-1</sup> characteristic of thiocyanates.<sup>8</sup> Like other nuclear aromatic thiocyanates, they were unaffected by ethanolic silver nitrate, whereas the compounds with an  $\alpha$ -thiocyanato-group in the side chain (see below) gave a precipitate readily.

Thiocyanogen chloride and naphthalene gave a single product, which was the known 1-thiocyanatonaphthalene, alternatively prepared from 1-naphthylamine. The reaction with anthracene was not so simple. Wood and Fieser treated this hydrocarbon in carbon tetrachloride with 1 or 4.4 mol. of thiocyanogen and in each case obtained 9,10-dithiocyanatoanthracene.<sup>5</sup> Under our conditions, slightly more than 1 mol. of thiocyanogen

<sup>7</sup> Strating and Backer, *Rec. Trav. chim.*, 1950, **69**, 638.

<sup>8</sup> Luskin, Gantert, and Craig, *J. Amer. Chem. Soc.*, 1956, **78**, 4965; Caldwell and Thompson, *Spectrochim. Acta*, 1958, **13**, 212; Lieber, Rao, and Ramchandran, *ibid.*, 1959, **13**, 296; Ham and Willis, *ibid.*, 1960, **16**, 279, 393; Svatek, Zahradnik, and Kjaer, *Acta Chem. Scand.*, 1959, **13**, 442.

chloride yielded a monosubstitution product (76%), m. p. 190°, presumably a purer sample of the 9-thiocyanatoanthracene, m. p. 181°, recorded in the literature.<sup>9</sup> The same compound resulted when larger proportions of the reagent were used, and it was then accompanied by substantial mixed fractions of undetermined composition. In one case, a by-product (7%) gave an analysis corresponding to that of a chlorothiocyanatoanthracene. It is well known that addition and elimination at the 9- and 10-positions complicate the substitution of anthracene by electrophilic reagents, and its reaction with thiocyanogen chloride needs further investigation from this point of view.

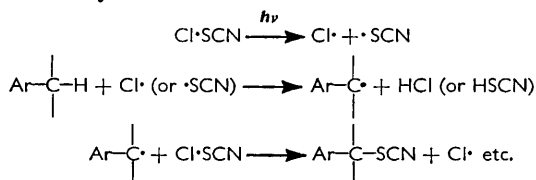
*Thiocyanation in a Substituent Alkyl Group.*—Whereas toluene gave no nuclear thiocyanate on prolonged treatment with thiocyanogen chloride in acetic acid at 40°, ultraviolet irradiation of the solution resulted in ready conversion of the hydrocarbon into benzyl thiocyanate. Thiocyanogen chloride absorbs light<sup>2</sup> from 450 to <280 m $\mu$ . The light source was a 250 w mercury-vapour lamp, the energy emitted from which included strong radiations at 365 and 436 m $\mu$ , and weaker radiations at 302, 313, 334, and 405 m $\mu$ . This novel homolytic reaction was applied to other arylalkyl hydrocarbons, in acetic acid or carbon tetrachloride solution, and some results of these experiments are shown in Table 2. As expected, *t*-butylbenzene failed to react, since it lacks an  $\alpha$ -hydrogen atom. In the cases of the other hydrocarbons, entry of the substituent at the  $\alpha$ -carbon atom was proved by comparing the products with those obtained by reaction of the corresponding  $\alpha$ -chloro- or  $\alpha$ -bromo-compounds with thiocyanate ion.

TABLE 2. Substitution of hydrocarbons by thiocyanogen chloride under ultraviolet irradiation.

Hydrocarbon (mol.)		Cl·SCN (1 mol. (molar concn.)	Solvent	Irradiation <sup>a</sup> at 35—45° (hr.)	Total Cl·SCN consumed (mol.)	Product isolated (mol.)
Toluene	(5)	0·154	AcOH	3	0·95	PhCH <sub>2</sub> ·SCN (0·63)
Ethylbenzene	.....	0·166	..	2	0·97	PhCHMe·SCN (0·68)
Isopropylbenzene	...	0·178	..	..	1·00	PhCMe <sub>2</sub> ·NCS (0·13) <sup>b</sup>
<i>t</i> -Butylbenzene <sup>c</sup>	...	0·1	CCl <sub>4</sub>	..	..	Nil
<i>m</i> -Xylene (i)	..	0·143	..	..	0·96	<i>m</i> -C <sub>6</sub> H <sub>4</sub> Me·CH <sub>2</sub> ·SCN (I) (0·69)
(ii)	..	0·144	AcOH	..	0·87	(I) (0·34) + 2,4,1-C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> ·SCN (II) (0·16)
(iii)	(0·5)	0·158	..	..	0·43	(I) (0·125) + (II) (0·050)
(iv)	..	0·143	..	.. <sup>d</sup>	0·96	(I) (0·18) + (II) (0·025)
Mesitylene	..	0·152	..	1	0·43	2,4,6,1-C <sub>6</sub> H <sub>2</sub> Me <sub>3</sub> ·SCN (0·23)
Diphenylmethane <sup>c</sup>	(5)	0·093	CCl <sub>4</sub>	4	0·75	CHPh <sub>2</sub> ·NCS (0·09)
Triphenylmethane <sup>c</sup>	(0·9)	0·119	..	1	0·92	CPh <sub>3</sub> ·NCS (0·64)

<sup>a</sup> The temperature is the result of thermal radiation from the lamp, modified by cooling. <sup>b</sup> Losses by decomposition occurred during isolation. <sup>c</sup> Experiments by R. S. Irwin, who also prepared these isothiocyanates with thiocyanogen (see text). <sup>d</sup> No cooling; the temperature rose to 95°.

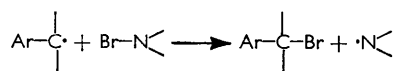
By adapting the usual chain mechanism used to represent homolytic side-chain halogenation, a reaction sequence may be written:



The most important feature in this sequence is the formation of a thiocyanate, and not a chloride, in the third step; the arylalkyl radical pairs with SCN, the more electropositive partner, in the fission of the Cl-SCN bond. This recalls Speier's observation that the substitution of toluene by bromine chloride under ultraviolet irradiation gives benzyl

<sup>9</sup> Footner and Smiles, *J.*, 1925, **127**, 2887.

bromide.<sup>10</sup> Walling has commented<sup>11</sup> that our present knowledge of the behaviour of radicals provides no obvious explanation of why the product obtained by Speier should be a bromide rather than a chloride. Further studies of homolytic substitutions by bromine chloride and similar mixed-halogen or halogen-pseudohalogen compounds would be valuable, though the course of such reactions might be complicated by the existence of inter-halogen equilibria, *e.g.*, of the type  $A_2 + B_2 \rightleftharpoons 2AB$ , which does not occur in solutions of thiocyanogen chloride. A reaction which is very appropriate for comparison with that of thiocyanogen chloride is the well-known side-chain bromination of arylalkyl hydrocarbons by *N*-bromosuccinimide, which is generally interpreted<sup>11</sup> as a homolytic chain reaction involving the step:



Here too the arylalkyl radical pairs with the more electropositive partner in the fission of the Br-N bond.

The reactions of thiocyanogen chloride solutions with *m*-xylene and with mesitylene, shown in Table 2, deserve comment, since they demonstrate that the reactants are rather delicately poised between side-chain substitution, promoted by the irradiation, and nuclear substitution, promoted by a polar solvent and by polar influences from the alkyl groups. Thus, when acetic acid is the solvent, thiocyanation occurs partly in the nucleus of *m*-xylene and entirely in the nucleus of mesitylene, in spite of irradiation. In general, reaction in acetic acid in darkness is the preferred means of nuclear substitution, while reaction in carbon tetrachloride under ultraviolet irradiation is the preferred means of side-chain substitution.

Another feature of Table 2 is that the product isolated may be an isothiocyanate instead of a thiocyanate. In certain cases (observations by R. S. Irwin) the isothiocyanate may be the only detectable product, as in the reaction with triphenylmethane, while in other cases, as with isopropylbenzene or diphenylmethane, it may be formed through the isomerisation,  $\text{R}\cdot\text{S}\cdot\text{C}:\text{N} \longrightarrow \text{R}\cdot\text{N}:\text{C}:\text{S}$ , of a thermally labile thiocyanate which is detectable as the initial product. Further information on the formation and structure of side-chain thiocyanation products has become available from later investigations.<sup>12</sup> Thiocyanates and isothiocyanates may be reliably and rapidly distinguished by their infrared absorption spectra.<sup>9</sup> For example, the spectrum of 1'-thiocyanatoethylbenzene showed a sharp peak at 2160  $\text{cm}^{-1}$ , characteristic of all the nuclear and side-chain thiocyanates examined, while the spectrum of distilled samples of 2-isothiocyanato-2-phenylpropane showed a strong and broad band at 2100  $\text{cm}^{-1}$ , with a shoulder at  $\sim 2000 \text{ cm}^{-1}$ , characteristic of isothiocyanates; in spectra of a sample of the ethylbenzene derivative which had been partially isomerised at 150°, or of a sample of the isopropylbenzene derivative before distillation, the band at 2100  $\text{cm}^{-1}$  was dominant, but the peak at 2160  $\text{cm}^{-1}$  was also clearly present.

#### EXPERIMENTAL

*Thiocyanations of the Aromatic Nucleus.*—Solutions of thiocyanogen chloride in acetic acid were prepared as described in Part III.<sup>1</sup> Thiocyanations of hydrocarbons and the recording of reaction rates were carried out as described for ethers and anilides in the same paper. Reaction flasks were usually rendered opaque with black paint. At the end of a thiocyanation, lead chloride (from the preparation of the reagent) was filtered off and the product was isolated by dilution of the solution with ice and water, followed, where necessary, by extraction with an organic solvent. To discover isomers or by-products, the isolated material was dissolved in light petroleum and chromatographed on a column of silica gel; 20–70 fractions, each of

<sup>10</sup> Speier, *J. Amer. Chem. Soc.*, 1951, **73**, 826.

<sup>11</sup> Walling, "Free Radicals in Solution," Wiley and Sons, New York, 1957.

<sup>12</sup> Bacon, Guy, and Irwin; and Bacon and Irwin, following papers.

volume ~70 ml., were collected. The following details refer to experiments summarised in Table 1.

*Toluene.* After treatment of toluene (3.40 g.) with the reagent, as shown in the Table, and removal of solvents, there remained an orange gum (0.97 g.) from which nothing could be separated by chromatography with light petroleum or benzene (cf. *m*-xylene).

*m*-Xylene. Under the conditions given in Table 1, 4.09 g. of *m*-xylene yielded 4.67 g. of a brown oil, which was chromatographed with benzene-light petroleum (3:7). Out of 40 fractions, nos. 7—25 yielded 2,4-dimethyl-1-thiocyanatobenzene (3.78 g., 60%), b. p. 133—134°/12 mm.,  $n_D^{25}$  1.5610 (Found: C, 66.4; H, 5.85; N, 8.4; S, 19.55.  $C_9H_9NS$  requires C, 66.25; H, 5.55; N, 8.6; S, 19.6%). A sample (1.0 g.) was reduced by treatment in ether (25 ml.) with lithium aluminium hydride (1.2 mol.).<sup>7</sup> When the vigorous reaction had subsided, the product was treated with water and then with 2*N*-sulphuric acid; the ether layer was evaporated, and the residual thiol was dissolved in ethanol, treated with 10% aqueous sodium hydroxide, and added to 1-chloro-2,4-dinitrobenzene (1.0 g.) in ethanol. The yellow precipitate was redissolved by warming, and sodium chloride was filtered off. On cooling, 2,4-dimethylphenyl 2,4-dinitrophenyl sulphide crystallised in yellow needles, m. p. 139—140° (Found: C, 55.4; H, 3.85; N, 9.2; S, 10.3.  $C_{14}H_{12}N_2O_4S$  requires C, 55.25; H, 4.0; N, 9.2; S, 10.5%).

For comparison, 2,4-dimethylaniline (0.1 mole) was dissolved in sulphuric acid (0.3 mole) and water (150 ml.) and diazotised. The ice-cold diazonium salt solution was added during 10 min. to a stirred ice-cold solution of potassium thiocyanate (0.5 mole) and ferric chloride (0.15 mole) in water (100 ml.). After being stirred for 2 hr. at 0° and 20 hr. at room temperature, the thick black suspension was kept for 1 hr. at 40°, which caused rapid evolution of nitrogen. Extraction, distillation, and further purification by chromatography yielded 2,4-dimethyl-1-thiocyanatobenzene (53%), b. p. 131—132°/10 mm.,  $n_D^{25}$  1.5610. It was reduced and the resulting thiol converted into 2,4-dimethylphenyl 2,4-dinitrophenyl sulphide, m. p. 139—140°, not depressed by admixture with the sample described above.

*Durene.* Under the conditions given in Table 1, 5.18 g. of durene yielded part of the product (2.42 g., 33%) as a pale yellow precipitate, m. p. 46—49°, when the solution was diluted. Recrystallisation from ethanol gave pure 2,3,5,6-tetramethyl-1-thiocyanatobenzene, m. p. 49—50° (Found: C, 69.25; H, 6.8; N, 7.25; S, 16.8.  $C_{11}H_{13}NS$  requires C, 69.1; H, 6.85; N, 7.35; S, 16.7%). A brown oil (3.36 g.) was obtained by ether-extraction of the diluted solution. The only product which this yielded when chromatographed with 1:1 benzene-light petroleum was additional 2,3,5,6-tetramethyl-1-thiocyanatobenzene (2.50 g., 34%).

*Mesitylene.* Under the conditions given for experiment (i) with mesitylene in Table 1, 4.58 g. of the hydrocarbon yielded practically pure 2,4,6-trimethyl-1-thiocyanatobenzene (6.10 g., 90%), m. p. 70—72°, when the solution was diluted. Recrystallisation from ethanol yielded the thiocyanate in needles, m. p. 71—72° (lit.,<sup>6</sup> 71—72°) (Found: C, 67.6; H, 6.25; N, 7.85; S, 18.6. Calc. for  $C_{10}H_{11}NS$ : C, 67.8; H, 6.25; N, 7.9; S, 18.1%). For comparison, nitromesitylene was reduced<sup>13</sup> to mesidine (78%), which was diazotised and treated with ferric thiocyanate as described for 2,4-dimethylaniline. After the evolution of nitrogen, the suspended solid was extracted into ether and the product (70%) was purified by chromatography and recrystallisation to give 2,4,6-trimethyl-1-thiocyanatobenzene, m. p. 71—72°, not depressed on admixture with the sample described above.

*Pentamethylbenzene.* Under the conditions given in Table 1, 5.71 g. of the hydrocarbon yielded the practically pure thiocyanate (7.61 g., 96%), m. p. 83—86°, on dilution of the solution. Recrystallisation from ethanol gave colourless prisms of pentamethylthiocyanatobenzene, m. p. 85—86° (Found: C, 70.1; H, 7.2; N, 6.7; S, 15.35.  $C_{12}H_{15}NS$  requires C, 70.2; H, 7.35; N, 6.8; S, 15.6%).

*Naphthalene.* Under the conditions given for experiment (i) with naphthalene in Table 1, 5.74 g. of the hydrocarbon yielded a crude product (6.26 g.) on dilution of the solution. Chromatography with 1:1 benzene-light petroleum gave unchanged naphthalene (1.85 g.), followed, in fractions nos. 6—17, by 1-thiocyanatonaphthalene (3.46 g., 42%), which, when recrystallised from ethanol, showed m. p. 54.5—55.5° (lit.,<sup>14</sup> 55°) (Found: C, 71.65; H, 3.65; N, 7.6; S, 17.25. Calc. for  $C_{11}H_7NS$ : C, 71.35; H, 3.8; N, 7.55; S, 17.3%). For comparison, it was prepared (62%) from 1-naphthylamine, by the procedure given for 2,4-dimethylaniline, and extracted into benzene. Purification by steam-distillation or chromatography, followed by

<sup>13</sup> Fierz-David and Mannhart, *Helv. Chim. Acta*, 1937, **20**, 1024.

<sup>14</sup> Challenger and Wilkinson, *J.*, 1922, **121**, 100.

recrystallisation from ethanol, gave 1-thiocyanatonaphthalene, m. p. 54.5—55.5°, not depressed on admixture with the sample described above.

*Anthracene.* Under the conditions given in Table 1, the anthracene (11.73 g.) dissolved slowly when added to the stirred acetic acid solution of thiocyanogen chloride, and a bright yellow crystalline precipitate rapidly separated. After filtration, this was extracted with hot acetone, evaporation of which left fairly pure 9-thiocyanatoanthracene (11.70 g., 76%), m. p. 182—187°, giving bright yellow needles, m. p. 189—190° (lit.,<sup>9</sup> 181°) on recrystallisation from acetone (Found: C, 76.4; H, 4.05; N, 6.05; S, 13.45. Calc. for C<sub>15</sub>H<sub>9</sub>NS: C, 76.6; H, 3.85; N, 5.95; S, 13.6%). Dilution of the filtered acetic acid solution with water gave a mixed, lower-melting product, difficult to purify.

Reaction was also carried out at 20° with 0.155M-thiocyanogen chloride (4 mol.). Titration showed the disappearance of 1.03 mol. of reagent in 10 min., and 2.01 mol. in 50 hr.; in a similar preparation at 40°, 3.04 mol. of reagent disappeared in 24 hr. As before, pure product was obtained only from the insoluble portion (2.87 g. from 3.24 g. of anthracene). Fractional crystallisation of this from acetone gave 9-thiocyanatoanthracene (0.96 g., 22%), m. p. and mixed m. p. 188—190°, and (probably) 9-chloro-10-thiocyanatoanthracene (0.36 g., 7%), m. p. 218—219° (Found: C, 66.6; H, 3.05; Cl, 13.0; N, 5.35; S, 12.15. C<sub>15</sub>H<sub>8</sub>ClNS requires C, 66.75; H, 3.0; Cl, 13.15; N, 5.2; S, 11.85%). Chromatography did not appear to be superior to recrystallisation for purification of the products.

*Thiocyanation with Ultraviolet Irradiation.*—Reactions were carried out (see Table 2) in gently stirred solutions in a Pyrex flask placed 8 cm. from a 250 w "Mazda" ME/D box-type mercury-vapour lamp. A water-cooled tube inside the flask counteracted the effect of thermal radiation from the lamp and kept the temperature of the solution at ~40°. The procedure was otherwise the same as that described above when acetic acid was the solvent. When reaction was to be carried out in carbon tetrachloride, thiocyanogen chloride was prepared by mixing solutions of chlorine and thiocyanogen in this solvent.<sup>2</sup> When the reaction was terminated, the solution was shaken with water to decompose and remove unchanged reagent, and the carbon tetrachloride was evaporated.

*Toluene.* Reaction with thiocyanogen chloride was carried out under the conditions given in Table 2. The solution was diluted with water and extracted with ether; solvent was evaporated, and the solid residue was chromatographed on silica gel with 2:3 benzene-light petroleum, 35 fractions being collected. Fractions 11—25 yielded benzyl thiocyanate (63%), m. p. 40—41° after recrystallisation from ethanol (lit.,<sup>9</sup> 41°) (Found: C, 64.6; H, 4.9; N, 9.0; S, 21.2. Calc. for C<sub>8</sub>H<sub>7</sub>NS: C, 64.4; H, 4.75; N, 9.4; S, 21.45%). Apart from a trace of oil (1%), containing no combined chlorine, in fractions 7—10, the column yielded no other product, even when eluted with more polar solvents. In a similar chromatographic treatment of a 1:1 mixture of benzyl thiocyanate and benzyl chloride, the latter separated quantitatively in fractions 3—4. The solvent mixture which had been removed from the reaction product was treated with cold aqueous sodium carbonate and fractionally distilled, but no benzyl chloride was found. From a similar solvent mixture, to which benzyl chloride had been added, the chloride was readily thus separated, and was estimated with ethanolic silver nitrate. Treatment of benzyl bromide with ammonium thiocyanate (2 mol.) in refluxing acetone yielded benzyl thiocyanate (95%), m. p. 40—41°, not depressed on admixture with the product obtained with thiocyanogen chloride.

*Ethylbenzene.* Reaction was carried out under the conditions given in Table 2 and the product was treated as described for toluene. From chromatography with benzene-light petroleum (1:1, changing to 7:3), 35 fractions were collected. A trace of oil (1%) was obtained from fractions 6 and 7, and 1'-thiocyanatoethylbenzene (68%) from fractions 8—16. On distillation, the latter showed b. p. 136—138°/11 mm. (lit.,<sup>15</sup> 157—159°/36 mm.), *n*<sub>D</sub><sup>25</sup> 1.5610, and gave an infrared absorption spectrum identical with that from an authentic sample (see below) (Found: C, 66.4; H, 5.35; N, 8.6; S, 19.4. Calc. for C<sub>9</sub>H<sub>9</sub>NS: C, 66.25; H, 5.55; N, 8.6; S, 19.6%). By a procedure similar to that described above for 2,4-dimethyl-1-thiocyanatobenzene, the 1'-thiocyanatoethylbenzene was converted into 2,4-dinitrophenyl 1-phenylethyl sulphide, which formed yellow prisms, m. p. 108—109° (lit.,<sup>16</sup> 109—110°) (Found: C, 55.4; H, 4.1; N, 9.15; S, 10.4. Calc. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>S: C, 55.25; H, 4.0; N, 9.2; S, 10.5%). For

<sup>15</sup> Wheeler and Johnson, *Amer. Chem. J.*, 1901, **26**, 202.

<sup>16</sup> Behring, *Annalen*, 1949, **564**, 219.

comparison, 1-phenylethanol was converted into 1'-bromoethylbenzene<sup>17</sup> (83%), and the latter was treated with ammonium thiocyanate (2 mol.) in refluxing acetone for 1 hr. to give 1'-thiocyanatoethylbenzene (94%), which was purified by distillation and chromatography. The pure sample, b. p. 136—138°/11 mm.,  $n_D^{25}$  1.5614, was likewise converted into 2,4-dinitrophenyl 1-phenylethyl sulphide, m. p. 108—109°, unchanged on admixture with the sample described above.

*Cumene.* Reaction carried out under the conditions shown in Table 2 gave a brown oil (91%), which was isolated as described for toluene. It was impure and unstable. When chromatographed on the usual silica-gel column with 1 : 1 benzene-light petroleum, 42% of the product (fractions 1—3) had a hydrocarbon-like odour, only 14% (fractions 7—18) was the desired thiocyanation product, and 27% (fractions 31—34, eluted with benzene-ether) was a viscous red oil. The fractions containing the thiocyanation product varied in refractive index and became deep yellow when kept, but yielded pure 2-isothiocyanato-2-phenylpropane on fractional distillation (Found: C, 67.8; H, 6.0; S, 18.1.  $C_{10}H_{11}NS$  requires C, 67.8; H, 6.25; N, 7.9; S, 18.05%). This was also obtained (b. p. 80°/0.2 mm.) by fractional distillation of the crude product. Alternatively, 2-phenylpropan-2-ol was treated with hydrogen chloride in benzene to give 2-chloro-2-phenylpropane,<sup>18</sup> which, after removal of solvent under reduced pressure, but without distillation, was kept for 3 days at room temperature with ammonium thiocyanate (2 mol.) in acetone. The solution was added to water and extracted with ether; the extract was washed with aqueous sodium hydrogen carbonate and evaporated, and the residue (68% yield) was distilled, to give 2-isothiocyanato-2-phenylpropane, b. p. 51—53°/0.04 mm. (Found: C, 68.1; H, 5.9; N, 7.85; S, 18.1%). Samples from the two sources gave the same infrared absorption spectrum, with a strong, broad band at 2100  $cm^{-1}$ , and each readily gave a precipitate with cold ethanolic silver nitrate.

*m-Xylene.* Under the conditions given for experiment (ii) with *m*-xylene in Table 2, the product, obtained by dilution of the acetic acid solution with water and ether-extraction, was a red-brown oil, which was chromatographed. Fractions 11—19, obtained with 3 : 7 benzene-light petroleum, yielded 2,4-dimethyl-1-thiocyanatobenzene (16%),  $n_D^{25}$  1.5610, identical with that resulting from reaction in darkness (see above). Fractions 25—35, obtained with 3 : 2 benzene-light petroleum, yielded 3-methylbenzyl thiocyanate (36%), b. p. 144—146°/10 mm. (lit.,<sup>15</sup> 147°/12 mm.),  $n_D^{25}$  1.5657 (Found: C, 66.2; H, 5.45; N, 8.6; S, 20.2. Calc. for  $C_9H_9NS$ : C, 66.25; H, 5.55; N, 8.6; S, 19.6%). Unlike the nuclear isomer, it readily gave a precipitate with warm ethanolic silver nitrate. Further elution with chloroform only yielded traces of intractable gums. The 3-methylbenzyl thiocyanate was reduced as described above and the resulting thiol was converted into 3-methylbenzyl 2,4-dinitrophenyl sulphide, which crystallised in yellow needles, m. p. 125—126° (Found: C, 55.6; H, 3.9; N, 9.55; S, 10.55.  $C_{14}H_{12}N_2O_4S$  requires C, 55.25; H, 4.0; N, 9.2; S, 10.5%).

For comparison, *m*-xylene (0.9 mole), *N*-bromosuccinimide (0.3 mole), benzoyl peroxide (1 g.), and carbon tetrachloride (100 ml.) were refluxed (7 hr.), giving 3-methylbenzyl bromide (63%), b. p. 103—105°/16 mm. (lit.,<sup>19</sup> 100—101°/14 mm.). This reacted (2 hr.) with ammonium thiocyanate (2 mol.) in boiling ethanol to give 3-methylbenzyl thiocyanate, identical in b. p.,  $n_D^{25}$ , and infrared absorption spectrum with the sample obtained by thiocyanation. Likewise, it gave the same 2,4-dinitrophenyl sulphide, m. p. and mixed m. p. 125—126°.

*Mesitylene.* Under the conditions given in Table 2, 4.58 g. of mesitylene gave 4.34 g. (64%) of crude product, m. p. 52—62°, which was chromatographed with 1 : 1 benzene-light petroleum. Fractions 5—11 contained 2,4,6-trimethylphenyl thiocyanate (45%), m. p. 71—72° after one recrystallisation. The only other product (5%) in the chromatogram was a semi-solid from fractions 13—19, which contained more trimethylphenyl thiocyanate, accompanied by a minute amount of an unidentified higher-melting product.

[By R. S. IRWIN] *Diphenylmethane.* Reaction with thiocyanogen chloride was carried out at 35° under conditions given in Table 2. Evaporation of solvent under reduced pressure left an impure liquid, in which the presence of a thiocyanate group was shown by a sharp peak at 2169  $cm^{-1}$  in the infrared absorption spectrum. Removal of excess of diphenylmethane at 74°/0.1 mm., followed by chromatography on silica gel with 1 : 9 benzene-light petroleum, gave diphenylmethyl isothiocyanate (9%), which crystallised from light petroleum in prisms, m. p.

<sup>17</sup> Hughes, Juliusburger, Scott, Topley, and Weiss, *J.*, 1936, 1173.

<sup>18</sup> Hoffmann, *J. Amer. Chem. Soc.*, 1929, 51, 2546.

<sup>19</sup> Titley, *J.*, 1926, 514.



57° (lit.,<sup>20</sup> 56.5—57.5°), and gave a strong broad band at 2060 cm.<sup>-1</sup> in the infrared absorption spectrum. It was identical with the product obtained by thiocyanation of diphenylmethane with thiocyanogen.<sup>4,12</sup>

[By R. S. IRWIN] *Triphenylmethane*. Reaction was carried out with thiocyanogen chloride at 37° under the conditions given in Table 2. The solvent was evaporated and the residue recrystallised from 1 : 1 ethanol-chloroform, to yield triphenylmethyl isothiocyanate (71%) in prisms, m. p. 137°. The sample was identical with that obtained by thiocyanation with thiocyanogen; <sup>4,12</sup> both showed a strong broad band at 2050 cm.<sup>-1</sup>.

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<sup>20</sup> Kaye, Kogon, and Parris, *J. Amer. Chem. Soc.*, 1952, **74**, 403.

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