# 471. *Thiocyanogen Chloride. Part V.*[1] *Heterolytic and Homolytic Thiocyanation of Alkylnaphthalenes.*

By R. G. R. BACON, R. G. GUY, and R. S. IRWIN.

The course of thiocyanation of 1-methyl-, 2-methyl-, 2-ethyl-, 2-isopropyl-, and 2-t-butyl-naphthalene by thiocyanogen chloride is attributed to competition between heterolytic substitution of the nucleus, promoted by a polar solvent, and homolytic substitution of an α-hydrogen atom in the alkyl group, promoted by light or a peroxide. Comparisons are made with known results of halogenation of methylnaphthalenes. Thiocyanation of 1-methylnaphthalene in acetic acid in darkness gives only 1-methyl-4-thiocyanatonaphthalene; in irradiated carbon tetrachloride it gives only 1-thiocyanatomethylnaphthalene; in acetic acid in the light it gives both; in carbon tetrachloride in darkness it gives neither. Similarly, in acetic acid in darkness the 2-alkylnaphthalenes give 2-alkyl-1-thiocyanatonaphthalenes; in irradiated carbon tetrachloride, 2-methyl- and 2-ethyl-naphthalene give the α-thiocyanato-derivatives, 2-isopropylnaphthalene gives the α-isothiocyanato-derivative, and 2-t-butylnaphthalene does not react. Structures of products are proved by alternative methods of synthesis, by infrared spectral characteristics, by reduction, and by other reactions. Mobility of the thiocyanato-group in 2-1′-thiocyanatoethylnaphthalene is displayed in its thermal isomerisation, and in its replacement by nucleophilic reagents.

PART IV[1] included observations on the reactivity of the naphthalene nucleus towards thiocyanogen chloride. Unsubstituted naphthalene was moderately reactive, whereas unsubstituted benzene was inert; and 1- and 2-methylnaphthalene were almost as reactive as 1,3,5-trimethylbenzene. Subsequent examination of the products from 1-methylnaphthalene showed that the methyl group was as readily thiocyanated as the nucleus. The contributions of nuclear and side-chain substitution have therefore been ascertained for this hydrocarbon under varying conditions (Table 1), and briefer investigations have been made with 2-methyl-, 2-ethyl-, 2-isopropyl-, and 2-t-butyl-naphthalene (Table 2).

Comparison of the 2-alkyl rather than the 1-alkyl homologues was convenient because the former series is the more readily accessible from Friedel–Crafts reactions. 2-Ethylnaphthalene is best prepared [2,3] by reduction of the crystalline 2-acetyl derivative, which

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[1] Part IV, preceding paper.

[2] Lévy, *Ann. Chim.* (*France*), 1938, **9**, 5.

[3] For preparations of alkylnaphthalenes, see Hickinbottom and Porter, *J. Inst. Petroleum*, 1949, **35**, 621; Luther and Wächter, *Chem. Ber.*, 1949, **82**, 161; Anderson, Smith, and Rallings, *J.*, 1953, 443; Wibaut, van Nes, and Stofberg, *Rec. Trav. chim.*, 1954, **73**, 501; Bailey, Smith, and Staveley, *J.*, 1956, 2731.

TABLE 1. *Reactions between* 1-*methylnaphthalene* (1 *mol.*) *and thiocyanogen chloride* (2 *mol.*) *in solution* (500 *ml.*), *yielding* 1-*methyl*-4-*thiocyanatonaphthalene* (I) *or* 1-*thiocyanatomethylnaphthalene* (II).

| | Cl·SCN concn. (M) | Solvent | Illumination, etc. | Temp. | Total time (hr.) | Total Cl·SCN consumed [a] (mol.) | Yield of nuclear isomer [b] (I) (mol.) | Yield of side-chain isomer [b] (II) (mol.) |
|---|---|---|---|---|---|---|---|---|
| (i) | 0·161 | AcOH | Darkness | 20° | 25 | 1·12 | 0·92 | Nil |
| (ii) | 0·132 | ,, | ,, | ,, | ,, | 1·10 | 0·88 | Nil |
| (iii) | 0·105 | $CCl_4$ | ,, | ,, | 124 | 0·66 | Nil | Nil |
| (iv) | 0·104 | ,, | Darkness; 0·2 g. $Bz_2O_2$ | 78 | 1 | 2·00 | Nil | 0·65 |
| (v) | 0·069 | AcOH | Lab. daylight [c] | 20 | 25 | 0·98 | 0·68 | 0·02 |
| (vi) | 0·136 | ,, | ,, | ,, | ,, | 1·16 | 0·71 | 0·08 |
| (vii) | 0·112 | ,, | ,, | ,, | ,, | 1·16 | 0·53 | 0·11 |
| (viii) | 0·093 | ,, | ,, | ,, | ,, | 1·16 | 0·44 | 0·32 |
| (ix) | 0·154 | ,, | ,, | 40 | 10 | 1·32 | 0·81 | 0·03 |
| (x) | 0·122 | ,, | W-filament lamp (500 w) | 26 | 3 | 1·00 | 0·64 | 0·08 |
| (xi) | 0·131 | ,, | do., plus daylight | 22 | ,, | 0·99 | 0·53 | 0·18 |
| (xii) | 0·100 | ,, | Hg-vapour lamp | 33 | 0·5 | 1·08 | 0·20 | 0·62 |
| (xiii) | 0·080 | ,, | ,, | 43 | 1·5 | 1·40 | 0·18 | 0·57 |
| (xiv) | 0·082 | ,, | ,, | 43 | 3 | 1·50 | 0·21 | 0·55 |
| (xv) | 0·126 | ,, | ,, | 39 | ,, | 1·46 | 0·21 | 0·52 |
| (xvi) | 0·250 | ,, | ,, | 43 | ,, | 1·64 | 0·46 | 0·46 |
| (xvii) | 0·092 $(SCN)_2$ | ,, | ,, | 49 | 7 | 0·58 $(SCN)_2$ | Nil | 0·40 |
| (xviii) | 0·107 | $CCl_4$ | ,, | 47 | 1·5 | 1·24 | Nil | 0·78 |
| (xix) | 0·090 $(SCN)_2$ | ,, | ,, | 47 | 3 | 0·92 $(SCN)_2$ | Nil | 0·50 |

[a] From iodometric titration. [b] Determined from infrared absorption curves and checked (expts. v—ix) by chromatographic separation (see Experimental section). [c] Expts. (v)—(ix) were performed in laboratory daylight during the months October—March.

TABLE 2. *Reaction between* 2-*alkylnaphthalenes and thiocyanogen chloride in solution* (500 *ml.*), *yielding* 2-*alkyl*-1-*thiocyanatonaphthalenes* (III) *or* 2-α-*thiocyanatoalkylnaphthalenes* (IV).

| | 2-Alkyl subst. | Cl·SCN Concn. (M) | Solvent | Cl·SCN/ $C_{10}H_7$Alk. (mol. ratio) | Illumination, etc. | Temp. | Total time (hr.) |
|---|---|---|---|---|---|---|---|
| (i) | Me | 0·157 | AcOH | 1 : 0·5 | Darkness | 20° | 34 |
| (ii) | ,, | 0·124 | ,, | ,, | Daylight | ,, | 30 |
| (iii) | ,, | 0·090 | $CCl_4$ | 1 : 5 | Hg lamp [c] | 37 | 5 |
| (iv) | Et | 0·187 | AcOH | 1 : 0·5 | Darkness | 20 | 70 |
| (v) | ,, | 0·090 | $CCl_4$ | 1 : 5 | Hg lamp [c] | 37 | 2·5 |
| (vi) | ,, | 0·112 | ,, | 1 : 0·5 | Darkness; 0·07 g. $Bz_2O_2$ | 78 | 4 |
| (vii) | Pr$^i$ | 0·095 | AcOH | ,, | Darkness | 20 | 250 |
| (viii) | ,, | 0·216 | $CHCl_3$ (125 ml.) | 1 : 2 | Daylight; 1·5 g. $AlCl_3$ | ,, | 1·5 |
| (ix) | ,, | 0·086 | $CCl_4$ | 1 : 0·55 | Hg lamp [c] | 37 | 2·3 |
| (x) | Bu$^t$ | 0·120 | AcOH | 1 : 0·5 | Darkness | 20 | 240 |
| (xi) | ,, | 0·105 | $CCl_4$ | 1 : 2 | Hg lamp [c] | 30 | 2 |

| | Cl·SCN consumed [a] (mol.) | Yield of nuclear isomer [b] (III) (%) | Yield of side-chain isomer [b] (IV) (%) |
|---|---|---|---|
| (i) | 0·57 | 81 | Nil |
| (ii) | 0·54 | 29 | 19 |
| (iii) | 0·70 | Nil | 25 |
| (iv) | 0·65 | 60 | Nil |
| (v) | 0·86 | Nil | 33 |
| (vi) | 0·52 | Nil | 30 |
| (vii) | 0·72 | 20 | Nil |
| (viii) | | 20 | Nil |
| (ix) | 0·75 | Nil | 10 [d] |
| (x) | 0·79 | 30 | Nil |
| (xi) | 0·05 | Nil | Nil |

[a] From iodometric titration. [b] Yields are calculated with reference to whichever reagent, Cl·SCN or alkylnaphthalene, was used in the lower proportion. [c] Irradiation by a 250 w " Mazda " ME/D mercury-vapour lamp (ref. 1). [d] This product was the isothiocyanate.

results from acetylation of naphthalene in nitrobenzene solution.[2,4] For 2-isopropylnaphthalene, an alkylation procedure used in a synthesis by Haworth and his co-workers [5] was followed; to check the structure, they also carried out a synthesis with a sample of 2-isopropylnaphthalene prepared from 2-acetylnaphthalene, and likewise (see below), when requiring an alternative route to the α-thiocyanation product of 2-isopropylnaphthalene, we based the second synthesis on the same ketone. 2-t-Butylnaphthalene has been frequently prepared by alkylation; distinction between the 2- and the 1-isomer has been made by Peters and his co-workers.[6] Since we have never isolated isomeric thiocyanation products other than those due to competitive reactivity of the nucleus and side chain, our hydrocarbon samples were not significantly heterogeneous.

The two products obtainable from 1-methylnaphthalene and thiocyanogen chloride (Table 1) were 1-methyl-4-thiocyanatonaphthalene and 1-thiocyanatomethylnaphthalene. The structure of the nuclear thiocyanate was proved, as in earlier cases,[1] by an alternative preparation from diazotised 4-methyl-1-naphthylamine. The other product was alternatively obtained by the reaction of 1-chloromethylnaphthalene with thiocyanate ion, as had been described in a patent.[7] The two isomers were quantitatively separated by chromatography with silica gel, on which the nuclear thiocyanate was the less strongly absorbed. Both showed the characteristic sharp absorption peak, due to thiocyanate, at 2160 cm.$^{-1}$ in their infrared spectra.[1] The thiocyanato-structure was also demonstrated chemically, in these and other cases, by conversion of the product into a thiol with lithium aluminium hydride,[1] or into a disulphide by alkaline fission of the S–CN bond.[8] The products from 1-methylnaphthalene were differentiated by the reactivity towards silver nitrate of the isomer containing the thiocyanatomethyl group and by the very different infrared absorption peaks which they showed in the 700—800 cm.$^{-1}$ region. The latter property was used for analysis of mixed thiocyanation products, and the results agreed closely with those obtained by the more tedious chromatographic separation of the isomers.

For the range of conditions summarised in Table 1, illumination and the nature of the solvent were the dominant factors controlling the product. In darkness, thiocyanation occurred wholly in the nucleus, and in high yield, if the solvent was acetic acid, but there was no reaction if the solvent was carbon tetrachloride. In daylight, and with acetic acid as solvent, nuclear thiocyanation was still the main result, but it was always accompanied by a minor and non-reproducible degree of substitution in the methyl group. Illumination by a tungsten-filament lamp had a similar effect to daylight. When a powerful mercury-vapour lamp [1] was used, reaction was substantially greater in the methyl group than in the nucleus, if the solvent was acetic acid, and it occurred entirely in the methyl group if the solvent was carbon tetrachloride. These facts suggest, as in the case of *m*-xylene already discussed,[1] that a homolytic, light-induced reaction in the methyl group is competing with a solvent-assisted heterolytic reaction in the nucleus. The beneficial effect of a polar solvent on nuclear substitutions by thiocyanogen chloride had been noted previously.[9] The homolytic character of the side-chain reaction is supported by the observation (expt. iv) that it could be induced in carbon tetrachloride in darkness if a peroxide was present to initiate radical chains. A further point of interest (expts. xvii, xix) is that thiocyanogen was successfully used in place of thiocyanogen chloride to achieve the homolytic reaction, though, in accordance with its known inferiority for heterolytic reactions,[1,9] thiocyanogen failed to attack the nucleus of 1-methylnaphthalene, even in

[4] Baddeley, *J.*, 1949, S 99; higher homologues were similarly prepared by Buu-Hoï and Cagniant, *Bull. Soc. chim. France*, 1945, **12**, 307.

[5] Haworth, Letsky, and Mavin, *J.*, 1932, 1784.

[6] (*a*) Bromby, Peters, and Rowe, *J.*, 1943, 144; (*b*) Contractor, Peters, and Rowe, *J.*, 1949, 1993; (*c*) Illingworth and Peters, *J.*, 1951, 1602.

[7] Jones and American Chemical Paint Co., U.S.P. 2,394,915/1946.

[8] Bacon, " Thiocyanates, Thiocyanogen, and Related Compounds," in " Organic Sulphur Compounds," Pergamon Press, London, Vol. I, in the press.

[9] Bacon and Guy *J.*, 1960, 318.

acetic acid solution. Homolytic reactions of thiocyanogen have been the subject of later investigations.[10,11]

2-Methylnaphthalene showed the same features as the 1-isomer in its reactions with thiocyanogen chloride (Table 2). The two products, 2-methyl-1-thiocyanatonaphthalene and 2-thiocyanatomethylnaphthalene, were characterised as already described for the 1-methylnaphthalene derivatives, and their identity was checked by the preparation of samples from 2-methyl-1-naphthylamine and 2-bromomethylnaphthalene respectively.

For substitutions of benzene derivatives, similarities between the behaviour of thiocyanogen chloride and that of the halogens have been noted.[1,9] Such similarities are likewise evident when the literature concerning halogenation of 1- and 2-methylnaphthalene is studied; information about their higher homologues is negligible. If nuclear chlorination or bromination is desired, unaccompanied by substitution in the methyl group, light should be excluded and high temperatures avoided.[12] Photobromination of 2-methylnaphthalene in carbon tetrachloride, with light of varying wavelength, was reported in one publication to cause only a small proportion of substitution in the methyl group,[13] but elsewhere 40—80% yields of the bromomethyl compound have been claimed.[14,15] *N*-Bromosuccinimide normally brominates the methyl group of 2-methylnaphthalene, but substitution can be transferred to the nucleus by the presence of traces of impurities.[14] It is well known that the efficacy of this reagent for aromatic side-chain substitution in general is greatly influenced by the solvent,[16] and recent observations in the benzene series show that, when the solvent is appropriately chosen, nuclear substitution may occur instead.[17] Results of the chlorination of 1-methylnaphthalene by *N*,2,4,6-tetrachloroacetanilide [18] show a marked similarity to those reported here for thiocyanogen chloride; in acetic acid, in the dark, 90% of the substitution was nuclear, but in carbon tetrachloride, with benzoyl peroxide present, it occurred entirely in the methyl group. All these reactions seem to involve competition between ionic and radical substitution processes, affecting the naphthalene nucleus and side chain respectively. However, this simple view might not survive a more detailed examination, for Mayo and Hardy's extensive study of the bromination of naphthalene [19] revealed unexpected complexity of mechanism.

Thiocyanation experiments with the higher homologues (Table 2) were confined to the use of acetic acid solutions in darkness for nuclear reaction, and of irradiated carbon tetrachloride solutions for reaction in the side chain. Under the former conditions, 2-ethylnaphthalene gave 2-ethyl-1-thiocyanatonaphthalene, and under the latter conditions, or with initiation by benzoyl peroxide instead of light, it gave 2-1′-thiocyanatoethylnaphthalene. The structures of these thiocyanates were proved by the presence of a sharp peak at 2150 cm.$^{-1}$ in their infrared absorption spectra; by reduction and other chemical reactions (see below); and by their synthesis from 2-ethyl-1-naphthylamine and 2-1′-bromoethylnaphthalene respectively. The 1-amine was obtained from 2-ethylnaphthalene by nitration and reduction, as described by Lévy,[2] who proved the intermediate to be 2-ethyl-1-nitronaphthalene by an unambiguous synthesis of 2-ethyl-1-naphthol, which he also prepared from the amine.

The nuclear thiocyanate from 2-isopropylnaphthalene, obtained in acetic acid in darkness, was considered, by analogy with the lower homologues, to be 2-isopropyl-1-thiocyanatonaphthalene. The yield was not improved when aluminium chloride was tried as

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[10] Bacon, Guy, Irwin, and Robinson, *Proc. Chem. Soc.*, 1959, 304.

[11] Bacon and Irwin, following paper.

[12] *E.g.*, Mayer and Sieglitz, *Ber.*, 1922, **55**, 1835; Robinson and Thompson, *J.*, 1932, 2015.

[13] King and Sampey, *J. Org. Chem.*, 1949, **14**, 470.

[14] Chapman and Williams, *J.*, 1952, 5044.

[15] Keene and Schofield, *J.*, 1957, 3181.

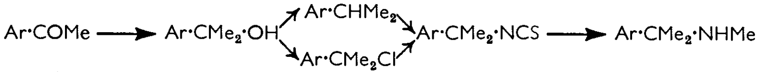
[16] Horner and Winkelmann, *Angew. Chem.*, 1959, **71**, 349.

[17] Ross, Finkelstein, and Petersen, *J. Amer. Chem. Soc.*, 1958, **80**, 4327.

[18] Ayad, Beard, Garwood, and Hickinbottom, *J.*, 1957, 2981.

[19] Mayo and Hardy, *J. Amer. Chem. Soc.*, 1952, **74**, 911.

catalyst.[20] The product of side-chain thiocyanation, obtained in irradiated carbon tetrachloride solution, was 2-isothiocyanato-2-2′-naphthylpropane. This was expected, since thiocyanation of isopropylbenzene had given an unstable thiocyanate, readily isomerising to the isothiocyanate during isolation,[1] and our general experience has been that the ease of an isomerisation, $>$CAr·SCN ⟶ $>$CAr·NCS, is increased when Ar is a naphthyl instead of a phenyl group.[8] The isothiocyanate structure was proved by the absence of the -SCN peak, and the presence of the broad -NCS peak at 2080 cm.$^{-1}$ in the infrared absorption spectrum; by the formation of an addition product, 2-$C_{10}H_7$·$CMe_2$·NH·CS·NR (NR = morpholino); and by reduction to 2-methylamino-2-2′-naphthylpropane with lithium aluminium hydride, under conditions described for phenyl isothiocyanate.[21] The reduction and an alternative synthesis of the isothiocyanate are shown in the annexed scheme.



(Ar = 2-$C_{10}H_7$)

2-2′-Naphthylpropan-2-ol was used as an intermediate both for the corresponding chloride and for an alternative preparation of 2-isopropylnaphthalene, which it gave on reductive dehydroxylation with Raney nickel.[22] The chloride was very reactive, and rapidly gave the isothiocyanate exclusively when treated with ammonium thiocyanate in acetone solution at room temperature. Regarded generally, replacements of halides can give a thiocyanate, an isothiocyanate, or a mixture of the two,[8] and the observed result again shows the influence of a constituent naphthyl group in favouring the iso-form.

The failure of 2-t-butylnaphthalene to undergo thiocyanation in irradiated carbon tetrachloride solution was expected, because of the absence of an α-hydrogen atom. The nuclear thiocyanation product, obtained in acetic acid solution, was considered, again by analogy, to be 2-t-butyl-1-thiocyanatonaphthalene. The 1-position in 2-t-butylnaphthalene, as in ethylnaphthalene,[2] is known to be the point of entry for a nitro-group,[6b] though sulphonation occurs in the other ring in both of these hydrocarbons.[2,6b,23] Comparison of the results in Table 2 suggests a decline in nuclear activity as the number of methyl groups attached to the α-carbon atom of the 2-alkyl group is increased; this could be due to steric hindrance at the 1-position.

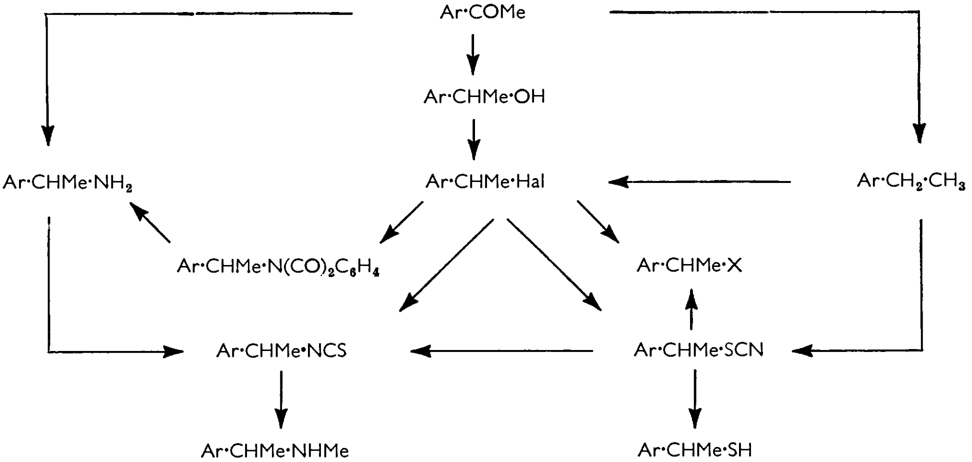
Finally, in the annexed scheme, we summarise a number of reactions involving thiocyanato- and other side-chain derivatives of 2-ethylnaphthalene.

The 1′-thiocyanate, obtained by homolytic thiocyanation, was also prepared, in high yield, by reaction of the 1′-bromo- or 1′-chloro-compound with ammonium thiocyanate in boiling acetone. When boiling ethanol was used, solvolysis intervened, and the resulting 1′-ethoxide was accompanied by both the 1′-thiocyanate and the 1′-isothiocyanate, separable by chromatography with silica gel, on which the isothiocyanate was the less strongly absorbed. As in some other cases in which a mixture of isomers results from reactions of halides with thiocyanate ion,[8] this result does not seem to be due to the thermal instability of the thiocyanato-form.

2-1′-Isothiocyanatoethylnaphthalene was also prepared through the dithiocarbamate,[24] obtained from 2-1′-aminoethylnaphthalene. The isothiocyanate and the thiocyanate were distinguished by infrared spectral characteristics and by reduction with lithium aluminium hydride, which gave the 1′-methylamino-derivative and the 1′-thiol, respectively. The thiocyanate was isomerised into the isothiocyanate at a distillation temperature of 140—150°; heating for 1 hr. in closed tubes at 120—150° resulted in a 70—80% yield of the isothiocyanate, the concentration of which was determined from the intensity of the very

[20] Cf. Söderbäck, *Acta Chem. Scand.*, 1954, **8**, 1851.
[21] Ried and Müller, *Chem. Ber.*, 1952, **85**, 470.
[22] Cf. Zderic, Bonner, and Greenlee, *J. Amer. Chem. Soc.*, 1957, **79**, 1696.
[23] Buu-Hoï, Le Behan, and Leroux, *J. Org. Chem.*, 1953, **18**, 582.
[24] Cf. *Org. Synth.*, Coll. Vol. III, p. 599.

strong band at 2095 cm.$^{-1}$ in the infrared absorption spectrum. Thermal instability was considerably greater in 2-1′-isothiocyanatoethylnaphthalene than in 1′-thiocyanatoethylbenzene, an observation which again shows the extra mobility conferred by a naphthyl substituent in comparison with a phenyl substituent. The thermally promoted isomerisation, R•SCN ⟶ R•NCS, is well known, but other manifestations of mobility in thiocyanates, such as replacements, R•SCN ⟶ RX, or elimination of HSCN, *i.e.*, reactions akin to those of halides, are not well known. Experiments incidentally carried out with 2-1′-thiocyanatoethylnaphthalene involved two such replacements, namely, conversion by thiourea into a thiouronium salt, and by boiling ethanol into the 1′-ethoxide. This type of reaction will be discussed in a later paper.



(Ar = 2-$C_{10}H_7$; Hal = Cl or Br; X = OEt or thiouronium picrate)

## EXPERIMENTAL

The procedure for thiocyanation in acetic acid solution was described in Parts III [9] and IV; [1] the procedure for photo-initiated thiocyanation was described in Part IV. Consumption of thiocyanogen chloride was determined, as previously described,[9,25] by iodometric titration of aliquot parts of the reaction mixtures. Products were isolated as described in the earlier papers.

*Estimation of Mixed Isomeric Thiocyanation Products.*—(*a*) When a reaction yielded two isomeric thiocyanates (Table 1; Table 2, expt. ii), these were separated by chromatography of the crude product on a column of silica gel with benzene–light petroleum, the proportion of benzene being gradually increased; further details are given for individual cases below. Fractions of volume ~70 ml. were collected.

(*b*) A method of analysis was developed for mixtures of 1-methyl-4-thiocyanatonaphthalene and 1-thiocyanatomethylnaphthalene (Table 1), based on differences in infrared absorption characteristics of these compounds. The former gives a strong, sharp peak at 752 cm.$^{-1}$ and the latter gives a strong, sharp peak at 722 cm.$^{-1}$. For each of these absorption peaks, optical density showed a strictly linear relation with concentration when examined over the range 1—160 mg. of thiocyanate per 5 ml. of carbon disulphide solution. The two peaks were clearly differentiated in solutions of the mixed isomers, and the concentrations of the two components, calculated from optical densities, were in close agreement ($\pm 1\%$) with the expected values in mixtures of known composition.

The presence of unchanged 1-methylnaphthalene interfered with this estimation and the hydrocarbon was accordingly eluted from the crude reaction product by adding a solution of the product in 3 : 1 benzene–light petroleum to a column of silica gel, and eluting the hydrocarbon with the same solvent mixture. The mixed hydrocarbon-free fractions were dissolved

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[25] Angus and Bacon, *J.*, 1958, 774; Bacon and Irwin, *J.*, 1958, 778.

in acetone, and an aliquot part of the solution, containing ~0·10 g. of product, was transferred to a graduated flask and evaporated. The volume was made up to 5 ml. in carbon disulphide for infrared spectroscopy, which was carried out in a Perkin–Elmer Model 21 spectrophotometer. The correspondence found between the chromatographic and the spectroscopic method of analysis is illustrated by the following yield figures, which refer to expt. (ix) in Table 1: isomer (I), 81% by chromatography, 82% by spectroscopy; isomer (II), 3% by chromatography 4% by spectroscopy.

*Thiocyanation of* 1-*Methylnaphthalene*.—The experiments (Table 1) were carried out with a pure, redistilled sample of the hydrocarbon, b. p. 121°/19 mm., $n_D^{25}$ 1·6148. It proved to be homogeneous when subjected to vapour-phase chromatography (Argon Chromatograph, W. G. Pye & Co.), under conditions which would have led to the detection of any 2-methylnaphthalene present in the sample. A typical procedure for the isolation of thiocyanation products is as follows. The reaction (expt. vii) was carried out on 3·89 g. of hydrocarbon in 500 ml. of an acetic acid solution of thiocyanogen chloride under the conditions given in the Table. Lead chloride,[9] left from the preparation of thiocyanogen chloride, was filtered off, and the solution was diluted with 3·5 l. of ice-water and kept overnight at 0°. Filtration yielded a light brown solid (4·53 g.), which was dissolved in benzene–light petroleum (1 : 1) for chromatography and eluted with the same solvent mixture. Fractions 2—4 yielded unchanged hydrocarbon (0·44 g.), and 7—21 yielded 1-*methyl*-4-*thiocyanatonaphthalene* (2·89 g., 53%), which, after one recrystallisation from ethanol, was obtained in colourless needles, m. p. 70—70·5°, not depressed on admixture with a sample prepared as described below (Found: C, 72·2; H, 4·4; N, 6·95; S, 15·8. $C_{12}H_9NS$ requires C, 72·35; H, 4·55; N, 7·0; S, 16·1%), $\lambda_{max.}$ 225 (log ε 4·74) and 292 mμ (log ε 3·94).

Elution was continued with benzene and yielded 1-thiocyanatomethylnaphthalene (0·61 g., 11%) in fractions 25—33. One recrystallisation from ethanol gave this isomer as prisms, m. p. 88—90° (lit.,[7] 91—91·5°), not depressed on admixture with a sample prepared as described below (Found: C, 71·95; H, 4·55; N, 6·85; S, 16·25%), $\lambda_{max.}$ 224 (log ε 4·76) and 284 mμ (log ε 3·92). It gave a precipitate with ethanolic silver nitrate and was converted, as described below, into di-1-naphthylmethyl disulphide, m. p. and mixed m. p. 108—109°.

For an alternative synthesis of 1-methyl-4-thiocyanatonaphthalene, nitration [26,27] of 1-methylnaphthalene (0·14 mole) gave a crude product (9 g.) which was purified by chromatography on alumina with 1 : 1 benzene–light petroleum, and by recrystallisation from ethanol, 1-methyl-4-nitronaphthalene being obtained in yellow needles (4·45 g., 17%), m. p. 64—67° (lit.,[26] 71—72°). This was reduced, as described for the 2-methyl-1-nitro-isomer,[28] with stannous chloride, and the resulting tin complex was decomposed, in solution, by aqueous potassium hydroxide, and 4-methyl-1-naphthylamine was obtained, on ether-extraction, as a brown solid (95%), m. p. 45—49° (lit.,[26] 51—52°). Its ethereal solution was treated with sulphuric acid to give the sulphate (80%), and the latter (0·02 mole) was diazotised and treated with ferric thiocyanate as previously described [1] for 2,4-dimethylaniline. The crude product (71%), obtained by ether-extraction, was purified by chromatography on silica gel with benzene–light petroleum (3 : 2, changing to 4 : 1), and by recrystallisation of fractions 9—17 (2·15 g., 57%) from ethanol; 1-methyl-4-thiocyanatonaphthalene was thus obtained in colourless needles, m. p. 70—70·5°.

For an alternative preparation of 1-thiocyanatomethylnaphthalene, an ethanolic solution of 1-chloromethylnaphthalene [29] and ammonium thiocyanate (1·1 mol.) was refluxed for 1·5 hr. Dilution with water precipitated the product in quantitative yield, and recrystallisation from ethanol gave prisms, m. p. 88—90°. For conversion into the disulphide, the thiocyanate (0·005 mole) in ethanol (40 ml.) was treated with sodium hydroxide (0·01 mole) in water (10 ml.) and ethanol (20 ml.), and the mixture was left overnight. The pale yellow precipitate (85%) was purified by chromatography with benzene–light petroleum (1 : 1) on silica gel; some yellow oil remained on the column and di-1-naphthylmethyl disulphide was obtained in colourless needles, m. p. 108—109° (lit.,[30] 108·5—109°) after recrystallisation from acetone (Found: C, 76·5; H, 5·25; S, 18·15. Calc. for $C_{22}H_{18}S_2$: C, 76·3; H, 5·25; S, 18·5%).

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[26] Lesser, *Annalen*, 1913, **402**, 1.
[27] Thompson, *J.*, 1932, 2310.
[28] Fierz-David and Mannhart, *Helv. Chim. Acta*, 1937, **20**, 1024.
[29] *Org. Synth.*, Coll. Vol. III, p. 195.
[30] Windus and Turley, *J. Amer. Leather Chemists' Assoc.*, 1938, **33**, 246.

*Thiocyanation of 2-Methylnaphthalene.*—(*a*) Under the conditions given for expt. (i) in Table 2, 5·56 g. of 2-methylnaphthalene yielded 7·31 g. of pale yellow solid, m. p. 85—90°, when the reaction mixture was diluted with ice-water. A portion of this (3·40 g.) was chromatographed with benzene–light petroleum (7 : 3), yielding, in fractions 2—3, unchanged hydrocarbon (0·27 g.), and, in fractions 5—12, 2-*methyl*-1-*thiocyanatonaphthalene* (2·95 g., corresponding to 81% yield), m. p. 99—102°; when recrystallised from ethanol it gave long, colourless needles, m. p. 101—102°, not depressed on admixture with a sample prepared as described below (Found: C, 72·4; H, 4·5; N, 6·65; S, 15·9. $C_{12}H_9NS$ requires C, 72·35; H, 4·55; N, 7·0; S, 16·1%), $\lambda_{max.}$ 224 (log ε 4·75) and 288 mμ (log ε 3·79). No other product was obtained from the column.

For an alternative synthesis of this compound, 2-methylnaphthalene was converted[28] into 2-methyl-1-nitronaphthalene (24%), and thence into 2-methyl-1-naphthylamine (82%), which was diazotised and treated with ferric thiocyanate as described[1] for 2,4-dimethylaniline. The crude product was chromatographed on silica gel with 3 : 2 benzene–light petroleum. The fractions containing 2-methyl-1-thiocyanatonaphthalene (56%) gave needles, m. p. 101—102°, when recrystallised from ethanol.

(*b*) Under the conditions given for expt. (ii) in Table 2, 4·39 g. of the hydrocarbon yielded 5·24 g. of crude product, 3·75 g. of which were chromatographed. Unchanged hydrocarbons (fractions 3—7; 1·04 g.) were eluted by 1 : 3 benzene–light petroleum; 2-methyl-1-thiocyanatonaphthalene (fractions 23—30; 1·29 g., corresponding to 29% yield) was eluted by 3 : 2 benzene–light petroleum; and 2-*thiocyanatomethylnaphthalene* (fractions 32—37; 0·83 g., 19% yield), m. p. 93—98°, was eluted by benzene. The 2-thiocyanatomethylnaphthalene was obtained in small, colourless needles, m. p. 101—101·5°, when recrystallised from carbon tetrachloride (Found: C, 72·2; H, 4·55; N, 6·8; S, 15·9. $C_{12}H_9NS$ requires C, 72·55; H, 4·55; N, 7·0; S, 16·1%), $\lambda_{max.}$ 225 (log ε 4·78) and 274 mμ (log ε 3·72). This compound showed no depression of m. p. on admixture with the sample prepared as described below, but showed a large depression in m. p. with the nuclear-substituted isomer, of similar m. p., described above. M. p. 101° was also shown by the sample of 2-thiocyanatomethylnaphthalene obtained by irradiation under the conditions given for expt. (iii) in Table 2.

For an alternative synthesis of 2-thiocyanatomethylnaphthalene, *N*-bromosuccinimide was used[31] to convert 2-methylnaphthalene into 2-bromomethylnaphthalene (65%), m. p. 52—55° (lit.,[31] 56°), which was treated with a slight excess of ammonium thiocyanate for 3 hr. in boiling ethanol. Dilution with water and recrystallisation of the precipitated product from carbon tetrachloride gave 2-thiocyanatomethylnaphthalene, m. p. 101—101·5°.

*Ethylnaphthalene.*—Reaction[2,4] between naphthalene (2 moles), acetyl chloride (2 moles), and anhydrous aluminium chloride (2 moles) in nitrobenzene (1 l.) gave 2-acetylnaphthalene, b. p. 128—130°/0·7 mm., which crystallised from light petroleum in prisms (47%), m. p. 52° (lit.,[2,4] 53·5°). The ketone was reduced by Huang-Minlon's method:[32] 2-acetylnaphthalene (0·8 mole), potassium hydroxide (2·8 moles), and 100% hydrazine hydrate (2·4 moles) in diethylene glycol (1100 ml.) were heated under reflux for 1·5 hr.; excess of hydrazine and water were then distilled off until the temperature of the liquid reached 200° (1·5 hr.) and refluxing was continued for 4 hr. The cooled solution was added to ice and water (4 l.), neutralised with sulphuric acid, and extracted with ether, 2-ethylnaphthalene being obtained (78%) with b. p. 118°/12 mm., $n_D^{25}$ 1·5987.

*Thiocyanation of 2-Ethylnaphthalene.*—(*a*) Under the conditions given for expt. (iv) in Table 2, 7·28 g. of 2-ethylnaphthalene gave 9·19 g. of a crude brown oil which was chromatographed on silica gel with benzene–light petroleum (1 : 9, changing to 1 : 1). This yielded 2-*ethyl*-1-*thiocyanatonaphthalene* (6·00 g., 60%), which crystallised from methanol in colourless, vesicant prisms, m. p. 54·5°, not depressed on admixture with a sample prepared as described below (Found: C, 73·15; H, 5·0; N, 6·2; S, 15·05. $C_{13}H_{11}NS$ requires C, 73·2; H, 5·2; N, 6·6; S, 15·0%). No other crystalline product was obtained from the chromatogram. By the procedure previously described,[1] the thiocyanate was characterised by reduction with lithium aluminium hydride and conversion of the resulting liquid thiol into 2-*ethyl*-1-*naphthyl* 2,4-*dinitrophenyl sulphide*, which crystallised from ethanol in yellow needles, m. p. 117° (Found: C, 60·9; H, 3·9; N, 7·9; S, 8·7. $C_{18}H_{14}N_2O_4S$ requires C, 61·0; H, 4·0; N, 7·9; S, 9·0%).

For an alternative synthesis of 2-ethyl-1-thiocyanatonaphthalene, the hydrocarbon (0·2 mole)

[31] Buu-Hoï, *Annalen*, 1944, **556**, 1.

[32] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

was converted [2] into 2-ethyl-1-nitronaphthalene (25%), m. p. 50·5° (lit.,[2] 49·5—50°), and thence into 2-ethyl-1-naphthylamine [2] (44%), which was diazotised and treated with ferric thiocyanate, as described [1] for 2,4-dimethylaniline. Decomposition was completed on the steam-bath, and the product was taken up in benzene, purified on a column of alumina, and recrystallised from methanol, which gave prisms (57%), m. p. 54°.

(*b*) After thiocyanation under the conditions given for expt. (v) in Table 2, solvent was removed and excess of hydrocarbon was distilled off at 165°/0·03 mm. The brown residue was chromatographed on silica gel with benzene–light petroleum; a 1 : 1 solvent mixture eluted 2-1′-*thiocyanatoethylnaphthalene* (33%), which recrystallised from light petroleum as prisms, m. p. 52·5°, not depressed on admixture with a sample prepared as described below (Found: C, 73·4; H, 5·1; N, 6·7; S, 15·3. $C_{13}H_{11}NS$ requires C, 73·2; H, 5·2; N, 6·6; S, 15·0%). The thiocyanation (expt. vi) involving benzoyl peroxide was conducted at the b. p. because only 5% consumption of reagent was observed in 4 hr. at 50°. When the experiment was repeated at the b. p. in the absence of peroxide most of the ethylnaphthalene was recovered unchanged and no thiocyanation product was observed.

The following paragraphs describe an alternative route to 2-1′-thiocyanatoethylnaphthalene, some reactions of the compound, and the preparation of other derivatives of ethylnaphthalene.

2-1′-*Hydroxyethylnaphthalene.*—2-Acetylnaphthalene (see above) (0·15 mole) in ether (50 ml.) was added during 20 min. to a slurry of lithium aluminium hydride (0·044 mole) in ether (60 ml.), and the mixture was refluxed for 1 hr. The product was decomposed by water and then by 10% sulphuric acid, and the ether solution was washed with aqueous sodium hydrogen carbonate and evaporated; 2-1′-hydroxyethylnaphthalene was obtained (24·1 g., 95%) as prisms, m. p. 72—74° (lit.,[33] 72°), by recrystallisation from light petroleum (Found: C, 83·7; H, 6·6. Calc. for $C_{12}H_{12}O$: C, 83·7; H, 7·0%).

2-1′-*Bromoethylnaphthalene.*—A solution of 2-1′-hydroxyethylnaphthalene (0·125 mole) in benzene (200 ml.) was treated with dry hydrogen bromide until an aqueous layer had separated (30 min.). The organic layer was washed with dilute aqueous sodium hydrogen carbonate, dried, and evaporated under reduced pressure. The residue of 2-1′-*bromoethylnaphthalene* recrystallised from light petroleum as prisms (23·5 g., 80%), m. p. 63—64° (Found: C, 61·1; H, 4·9; Br, 33·85. $C_{12}H_{11}Br$ requires C, 61·3; H, 4·7; Br, 34·0%). Alternatively, a solution of 2-ethylnaphthalene (0·1 mole), *N*-bromosuccinimide (0·1 mole), and benzoyl peroxide (0·1 g.) in dry carbon tetrachloride (80 ml.) was refluxed for 4·5 hr., and the warm solution was filtered and evaporated, giving 2-1′-bromoethylnaphthalene (91%), m. p. 63°, on recrystallisation. The bromide was treated with an equal weight of thiourea for 20 min. in boiling ethanol; after addition of picric acid and cooling, S-(1-2′-*naphthylethyl*)*thiouronium picrate* separated, and recrystallised from aqueous ethanol as yellow needles, m. p. 202° (Found: C, 50·0; H, 4·0; N, 15·3; S, 6·8. $C_{19}H_{17}N_5O_7S$ requires C, 49·7; H, 3·7; N, 15·25; S, 7·0%).

2-1′-*Chloroethylnaphthalene.*—Treatment of 2-1′-hydroxyethylnaphthalene (0·15 mole) with dry hydrogen chloride, as described for the bromide, gave 2-1′-*chloroethylnaphthalene* (24·5 g., 86%), crystallising from light petroleum in prisms, m. p. 67° (Found: C, 75·6; H, 5·7. $C_{12}H_{11}Cl$ requires C, 75·6; H, 5·8%). It likewise gave the thiouronium picrate, m. p. 202°.

2-1′-*Thiocyanatoethylnaphthalene.*—Ammonium thiocyanate (0·225 mole) was heated with 2-1′-bromoethylnaphthalene (0·075 mole) in acetone (125 ml.) for 1 hr. under reflux. After addition of the mixture to water, extraction with ether gave 2-1′-thiocyanatoethylnaphthalene (12 g., 75%), m. p. 52·5°, after recrystallisation from light petroleum. 2-1′-Chloroethylnaphthalene and ammonium thiocyanate (3 mol.) likewise gave the 2-1′-thiocyanate (90%), after 3·5 hr. in refluxing acetone. The thiocyanate showed a strong, sharp peak at 2150 cm.$^{-1}$ in the infrared absorption spectrum (5% solution in carbon tetrachloride). When treated with thiourea, under conditions used for the bromide (see above), it was converted into *S*-(1-2′-naphthylethyl)thiouronium picrate, m. p. and mixed m. p. 202°. When reduced with lithium aluminium hydride (1·2 mol.), the thiocyanate formed 1-2′-*naphthylethane*-1-*thiol* (96%), b. p. 122°/0·7 mm., prisms, m. p. 37—38° (Found: C, 76·35; H, 6·8; S, 16·7. $C_{12}H_{12}S$ requires C, 76·6; H, 6·4; S, 17·0%). The thiol could not be converted into a 2,4-dinitrophenyl sulphide; it formed unstable lead and mercury derivatives.

2-1′-*Aminoethylnaphthalene.*—Reaction was carried out between potassium phthalimide [34]

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[33] Lund, *Ber.*, 1937, **70**, 1520.

[34] Hale and Britton, *J. Amer. Chem. Soc.*, 1919, **41**, 844.

(0·12 mole) and 2-1′-bromoethylnaphthalene (0·11 mole), the solvent being dimethylformamide (90 ml.) as recommended [35] for this type of replacement. After brisk stirring at 70° for 2 hr., the mixture was cooled, and chloroform (135 ml.) was added, followed by water (450 ml.). The chloroform layer was washed with 0·2N-aqueous sodium hydroxide, dried, and evaporated. On trituration with light petroleum the residual gum yielded *2-1′-phthalimidoethylnaphthalene*, which crystallised from ethanol in prisms (24·5 g., 74%), m. p. 100·5—102° (Found: C, 79·8; H, 5·25. $C_{20}H_{15}NO_2$ requires C, 79·8; H, 5·0%). This was decomposed by Ing and Manske's method,[36] giving the liquid 2-1′-aminoethylnaphthalene (80%), which formed the hydrochloride, m. p. 200—202° (from water) (lit.,[37] 198—199°). With benzoyl chloride and aqueous sodium hydroxide it gave *2-1′-benzamidoethylnaphthalene*, m. p. 151·5° on recrystallisation from aqueous ethanol (Found: C, 83·1; H, 6·3; N, 4·95. $C_{19}H_{17}NO$ requires C, 82·9; H, 6·2; N, 5·1%). Alternatively, 2-1′-aminoethylnaphthalene was prepared from 2-acetylnaphthalene by the known [37] Leuckart method and isolated as the hydrochloride (52%), m. p. 200—202°.

*2-1′-Isothiocyanatoethylnaphthalene*.—(*a*) 2-1′-Aminoethylnaphthalene (6·80 g., 0·04 mole) and sodium hydroxide (0·04 mole) in water (7 ml.) were cooled to 10° and carbon disulphide (0·04 mole) was added with vigorous stirring during 30 min., accompanied by water (40 ml.), so that the resulting dithiocarbamate derivative was maintained as a slurry. This was stirred for 30 min. at 60° and was then decomposed with ethyl chloroformate (0·04 mole) at 35—40°, as described for methyl isothiocyanate.[24] *2-1′-Isothiocyanatoethylnaphthalene* was extracted with ether and obtained as prisms (6·3 g., 73%) in one recrystallisation from light petroleum; two more recrystallisations removed yellow impurity and raised the m. p. to 49—50·5° (Found: C, 73·6; H, 5·5; N, 6·4; S, 15·3. $C_{13}H_{11}NS$ requires C, 73·2; H, 5·2; N, 6·6; S, 15·0%). The infrared absorption spectrum (5% solution in carbon tetrachloride) showed a very strong, broad band at 2090 cm.$^{-1}$. The isothiocyanate (1·00 g.) was treated with lithium aluminium hydride [21] (1·8 mol.) for 30 min. in boiling ether (25 ml.) and yielded *2-1′-methylaminoethylnaphthalene* (0·76 g., 89%), b. p. 97°/0·5 mm. (Found: C, 83·5; H, 8·2; N, 7·5. $C_{13}H_{15}N$ requires C, 84·3; H, 8·1; N, 7·6%). It was characterised by conversion with 1-naphthyl isocyanate into N-*methyl*-N-1-2′-*naphthylethyl*-N′-1″-*naphthylurea*, which crystallised from ethanol in prisms, m. p. 154—155° (Found: C, 81·5; H, 6·2; N, 7·6. $C_{24}H_{22}N_2O$ requires C, 81·3; H, 6·2; N, 7·9%).

(*b*) A solution of 2-1′-chloroethylnaphthalene (0·12 mole) and ammonium thiocyanate (0·24 mole) in ethanol (200 ml.) was boiled under reflux for 3·5 hr. The product was added to water and extracted with ether, and the extract was washed with aqueous sodium hydrogen carbonate, dried, and evaporated. The residue was a pale green oil, which failed to yield crystals at −20°. When a portion was chromatographed on silica gel, 70% of the sample was recovered. The fractions (23%), obtained with 5 : 95 benzene–light petroleum, consisted of nearly pure 2-1′-isothiocyanatoethylnaphthalene, m. p. and mixed m. p. 49—50° after recrystallisation, with characteristic infrared absorption spectrum. Elution with 10 : 90 benzene–light petroleum then gave oils, and further elution with a 30 : 70 mixture gave partly crystalline fractions, from which 2-1′-thiocyanatoethylnaphthalene (13%) was obtained by crystallisation from light petroleum. The m. p. (48—49°) was a little low, but not depressed by authentic material, and the sample showed the characteristic thiocyanate band in the infrared absorption spectrum at 2160 cm.$^{-1}$. Distillation of the bulk of the reaction product yielded mainly 2-1′-ethoxyethylnaphthalene (see below), followed by a fraction which solidified and was fairly pure 2-1′-isothiocyanatoethylnaphthalene.

(*c*) Pure 2-1′-thiocyanatoethylnaphthalene (4·0 g.) was isomerised by four distillations under reduced pressure in a small-scale apparatus heated by a bath at 200°. The b. p. rose from ~140°/0·4 mm. and became practically constant at ~150°/0·4 mm. The distillate solidified and was purified by chromatography with 5 : 95 benzene–light petroleum on silica gel, which yielded 2·1 g. of 2-1′-isothiocyanatoethylnaphthalene, m. p. and mixed m. p. 48—50°.

(*d*) Solutions of pure 2-1′-isothiocyanatoethylnaphthalene in carbon tetrachloride showed a linear relationship between their concentration and the optical density of the strong, broad isothiocyanate band at 2096 cm.$^{-1}$ in the infrared absorption spectrum. This was used to

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[35] Sheehan and Bolhofer, *J. Amer. Chem. Soc.*, 1950, **72**, 2786.

[36] Ing and Manske, *J.*, 1926, 2348.

[37] Ingersoll, Brown, Kim, Beauchamp, and Jennings, *J. Amer. Chem. Soc.*, 1936, **58**, 1808; cf. Moore, *Org. Reactions*, **5**, 301.

determine the amount of isothiocyanate formed by keeping samples of 2-1′-thiocyanatoethylnaphthalene for 1 hr. in stoppered tubes in a constant-temperature bath. At 120° the isothiocyanate content of the product was 73% and at 150° it was 77%; some decomposition occurred above ~120°. Similar experiments with 1-thiocyanatoethylbenzene [1] showed the content of 1-isothiocyanatoethylbenzene after 1 hr. to be 7% at 120°, and 42% at 150°.

2-1′-*Ethoxyethylnaphthalene*.—(*a*) The liquid fractions obtained by distillation of the mixed product from the reaction of 2-1′-chloroethylnaphthalene with ethanolic ammonium thiocyanate (see above) were redistilled, to give 2-1′-ethoxyethylnaphthalene, b. p. 111—113°/0·6 mm. (lit.,[38] 145—148°/16 mm.) (Found: C, 84·0; H, 7·7. Calc. for $C_{14}H_{16}O$: C, 84·0; H, 8·0%).

(*b*) A solution of 2-1′-bromoethylnaphthalene (2·0 g.) in ethanol (25 ml.) was refluxed for 12 hr. The distilled product was bromine-free and fairly homogeneous; redistillation afforded a sample of the 1′-ethoxide, b. p. 81—83°/0·25 mm.

(*c*) 2-1′-Thiocyanatoethylnaphthalene, b. p. $>140°$/0·4 mm. (see above), was treated with ethanol as in (*b*). Distillation afforded a sample of the 1′-ethoxide, b. p. 80—81°/0·15 mm.

2-*Isopropylnaphthalene*.—A poor yield was obtained by following a described method,[5] involving anhydrous aluminium chloride (40 g.), naphthalene (3 moles), and isopropyl bromide (2 moles), in the absence of a solvent; redistillation of the product gave 2-isopropylnaphthalene, b. p. 134·5—136°/14 mm. (lit.,[5] 130—135°/12 mm.). Alternatively, 2-acetylnaphthalene (see above; 1 mole) was converted by methylmagnesium iodide into 2-2′-naphthylpropan-2-ol (65%), which crystallised from light petroleum in prisms, m. p. 63—65° (lit.,[39] 65—65·5°). In a small-scale preparation, this alcohol (3·0 g.) was heated under reflux in ethanol with 4 times its weight of Raney nickel, as described for the reductive dehydroxylation of other alcohols; [22] 2-isopropylnaphthalene (65%), b. p. 137—139°/15 mm., was obtained on distillation.

*Thiocyanation of* 2-*Isopropylnaphthalene*.—(*a*) After prolonged reaction in acetic acid, as shown for expt. (vii) in Table 2, the crude product was isolated by addition to water, ether-extraction, and removal of solvent under reduced pressure. Passage of a solution of the product in 19 : 1 benzene–light petroleum down a column of silica gel removed resin, and distillation yielded 2-*isopropyl*-1-*thiocyanatonaphthalene* (1·1 g., 20%), a viscous, vesicant liquid, collected at 124—137°/0·02 mm.; a redistilled sample had b. p. 107°/3 × $10^{-4}$ mm. (Found: C, 74·0; H, 5·8; N, 6·3; S, 13·75. $C_{14}H_{13}NS$ requires C, 74·0; H, 5·7; N, 6·2; S, 14·1%). The infrared absorption spectrum (liquid film) showed a sharp peak at 2160 cm.$^{-1}$ characteristic of a thiocyanate. Reaction with excess of lithium aluminium hydride (1·8 mol.) yielded a liquid with a thiol-like odour, which gave only gum with 1-chloro-2,4-dinitrobenzene. No amine was detected in the reduction product. For the catalysed thiocyanation (expt. viii in Table 2; vol. of solution reduced to 125 ml.) the procedure was similar to that used by Söderbäck [20] for reactions with thiocyanogen. The aluminium chloride, dissolved in a few ml. of ether, was added to the 2-isopropylnaphthalene and thiocyanogen chloride in chloroform, and the mixture was briefly heated to 55° and left for 1·5 hr. at room temperature. Much yellow polymer was formed. The solution was washed with water and distilled; unchanged hydrocarbon was obtained, followed by 2-isopropyl-1-thiocyanatonaphthalene (1·1 g., 20%); the latter was redistilled at 112—113°/5 × $10^{-4}$ mm. and showed the same infrared spectral characteristics as the sample described above (Found: C, 73·9; H, 5·9; N, 6·2; S, 13·7%).

(*b*) Thiocyanation under the conditions given for expt. (ix) in Table 2, followed by removal of solvent below 40°, left a brown semi-solid residue, purified by elution through a column of silica gel with 1 l. of light petroleum. This yielded crude 2-*isothiocyanato*-2-2′-*naphthylpropane* as a liquid (2·0 g.) giving colourless prisms (0·5 g., 10%), m. p. 45—46°, by crystallisation from a light petroleum solution cooled to $-20°$; there was no depression in m. p. on admixture with a sample prepared as described below (Found: N, 6·2; S, 14·2. $C_{14}H_{13}NS$ requires N, 6·2; S, 14·1%). Neither the crude nor the purified product showed infrared spectral characteristics of a thiocyanate, but both showed the very strong, broad isothiocyanate band at 2078 cm.$^{-1}$ (5% carbon disulphide solution).

For comparison, 2-2′-naphthylpropan-2-ol (see above) was treated in benzene solution with dry hydrogen chloride, and solvent was removed under reduced pressure to yield 2-chloro-2-2′-naphthylpropane, which solidified on cooling and readily lost hydrogen chloride. Without

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[38] Balfe, Kenyon, and Searle, *J.*, 1951, 380.

[39] Fieser and Chang, *J. Amer. Chem. Soc.*, 1942, **64**, 2043.

purification, the chloride (0·15 mole) was treated with ammonium thiocyanate (0·45 mole) in acetone (200 ml.) at room temperature; ammonium chloride was immediately precipitated. After being left overnight, the solution was added to water, the mixture cooled, and the precipitated 2-isothiocyanato-2-2′-naphthylpropane recrystallised from light petroleum as prisms (23 g., 67%), m. p. 45·5—46°, which showed a strong broad band at 2070 cm.$^{-1}$ in the infrared absorption spectrum, but none attributable to thiocyanate. Treatment of the isothiocyanate with morpholine gave N-[N′-(1-*methyl*-1-2′-*naphthylethyl*)*thiocarbamoyl*]*morpholine*, recrystallising from benzene in prisms, m. p. 137·5—138·5° (Found: C, 69·0; H, 6·7; N, 8·7; S, 10·6. $C_{18}H_{22}N_2OS$ requires C, 68·8; H, 7·0; N, 8·9; S, 10·2%). By reduction of the isothiocyanate (2·0 g.) with lithium aluminium hydride (1·8 mol.), 2-*methylamino*-2-2′-*naphthylpropane* was obtained as a colourless liquid (1·46 g., 85%), b. p. 103°/0·2 mm. (Found: C, 84·9; H, 8·4; N, 7·0. $C_{14}H_{17}N$ requires C, 84·5; H, 8·4; N, 7·1%). With 1-naphthyl isocyanate, the amine gave the urea derivative, crystallising from chloroform in prisms, m. p. 190—192°.

*Thiocyanation of t-Butylnaphthalene.*—Reaction by a known method [6a] between naphthalene, t-butyl chloride, and anhydrous zinc chloride gave 2-t-butylnaphthalene in poor yield, b. p. 143—145°/27 mm. (lit.,[6a] 137—139°/17 mm.). Thiocyanation under the conditions given for expt. (x) in Table 2, followed by addition to water, extraction with ether, and distillation, gave 2-t-*butyl*-1-*thiocyanatonaphthalene* (1·75 g., 30%) as a pale yellow liquid, b. p. 140—142°/0·65 mm. (Found: C, 74·4; H, 6·3; N, 5·65; S, 12·8. $C_{15}H_{15}NS$ requires C, 74·7; H, 6·2; N, 5·8; S, 13·3%). The infrared absorption spectrum (liquid film) showed a fairly strong sharp peak at 2162 cm.$^{-1}$, due to thiocyanate. Reduction with lithium aluminium hydride (1·8 mol.) gave a liquid, with thiol-like odour, which formed only a gum in reaction with 1-chloro-2,4-dinitrobenzene.

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THE QUEEN'S UNIVERSITY, BELFAST.

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