472. *Thiocyanogen, Thiocyanates, and Isothiocyanates. Part I. Homolytic Substitution in Arylalkyl Hydrocarbons by Thiocyanogen.*

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Like thiocyanogen chloride, thiocyanogen undergoes homolysis in organic solvents when irradiated by a mercury-vapour lamp, and the resulting thiocyanogen radicals cause substitution of hydrogen on the α-carbon atom of arylalkyl hydrocarbons; the fastest reactions have been obtained in carbon tetrachloride. Toluene, 2-methylnaphthalene, ethylbenzene, 2-ethylnaphthalene, isobutylbenzene, and bibenzyl give thiocyanates; isopropylbenzene and diphenylmethane give thiocyanates which isomerise to isothiocyanates during isolation; from s-butylbenzene, triphenylmethane, 2-isopropylnaphthalene, and retene, only isothiocyanates are isolated. Aspects of S–S bond fission and of the isomerisation, R·SCN $\longrightarrow$ R·NCS, are discussed. Decomposition to olefins is a property of some secondary and tertiary thiocyanates and isothiocyanates.

In previous papers we have discussed properties of thiocyanogen monochloride,[1] thiocyanogen trichloride,[2] and various organic thiocyanates, isothiocyanates, or dichlorothiocyanates prepared by means of these reagents. Some observations made during this work have suggested directions in which the chemistry of the parent thiocyanogen, a compound well-known for its pseudohalogen character,[3,4] could be extended. During experiments

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[1] Bacon, Guy, and Irwin, preceding paper.
[2] Bacon and Irwin, *J.*, 1960, 5079.
[3] Wood, *Org. Reactions*, 1946, **3**, 240.
[4] Kaufmann, in "Newer Methods of Preparative Organic Chemistry," Interscience Publ. Inc., New York, 1948.

in which photo-initiated homolysis of thiocyanogen chloride was used for thiocyanation of the methyl group in 1-methylnaphthalene,[1] thiocyanogen was found to function similarly. As a result of such observations, it was suggested [5] that an important but previously unrecognised property of thiocyanogen is an ability to undergo homolysis, analogous to that of chlorine or bromine, giving thiocyanogen radicals: $NCS{\cdot}SCN \longrightarrow 2NCS{\cdot}$. The present paper describes the application of this property in the preparation of thiocyanates or isothiocyanates by substitution at the α-position in twelve arylalkyl hydrocarbons.

The thiocyanations, summarised in the Table, were carried out close to a 250 w mercury-vapour lamp. The energy emitted by this source included intense radiation at 365 mμ and less intense radiations at 302, 313, 334, and 405 mμ; absorption of light by solutions of thiocyanogen occurs from 400 to <280 mμ, with a maximum at 300 mμ.[6] Because of thermal radiation from the lamp, it was convenient to conduct reactions at ~35°. Under such conditions, solutions (~0·1M) of thiocyanogen in carbon tetrachloride declined in iodometric titre at the rate of about 1% in 1—2 hr., and formed the customary precipitate of polymer. The rate of decomposition was nearly the same for thiocyanogen solutions containing t-butylbenzene or 2-t-butylnaphthalene, which, having no α-hydrogen atoms, do not undergo homolytic thiocyanation.[1] This degree of stability was unexpected, in view of reports [3] of the ready polymerisation of thiocyanogen by sunlight.

Light-induced thiocyanation, by 0·1M-*thiocyanogen, at* 35°,[a] *of arylalkyl hydrocarbons:*
$Ar{\cdot}CHRR' \longrightarrow Ar{\cdot}CRR'{\cdot}SCN$ *or* $Ar{\cdot}CRR'{\cdot}NCS$.

Hydrocarbon	Hydrocarbon (mol.) per mol. of $(SCN)_2$	Solvent	Reaction time (hr.)	Total $(SCN)_2$ decomp. (%) [b]	$(SCN)_2$ (%) accounted for by isolated product [c]	Product
None	—	CCl_4	3	2	—	—
$Ph{\cdot}CH_3$ (i)	10	,,	3·5	60	31	Thiocyanate
(ii)	5	AcOH	4·5	12	7	,,
(iii)	100	PhMe	2·5	87	49	,,
$Ph{\cdot}CH_2Me$ (i)	5	CCl_4	1·5	98	89	,,
(ii)	,,	AcOH	3·0	54	34	,,
$Ph{\cdot}CHMe_2$ (i)	,,	CCl_4	0·5	97	82	Isothiocyanate
(ii)	,,	AcOH	3·0	47	18	,,
$Ph{\cdot}CMe_3$	,,	CCl_4	2·5	5	—	None
$Ph{\cdot}CH_2Pr^i$	4	,,	3·0	83	70	Thiocyanate
$Ph{\cdot}CHMeEt$	,,	,,	1·25	98	58	Isothiocyanate
$2\text{-}C_{10}H_7{\cdot}CH_3$	5	,,	6·0	64	25	Thiocyanate
$2\text{-}C_{10}H_7{\cdot}CH_2Me$	,,	,,	2·5	95	51	,,
$2\text{-}C_{10}H_7{\cdot}CHMe_2$	0·5	,,	2·3	64	5 [d]	Isothiocyanate
$2\text{-}C_{10}H_7{\cdot}CMe_3$	2	,,	2·0	5	—	None
$Ph{\cdot}CH_2{\cdot}CH_2Ph$	1	,,	3·5	74	61	Thiocyanate
CH_2Ph_2	5	,,	3·0	91	49	Isothiocyanate
$CHPh_3$	1	,,	0·5	90	77	,,
Retene	0·5	,,	4·0	50	15 [e]	,,

[a] Volume of solutions, 500 ml.; variation in concentration, 0·079 to 0·123M; variation in temperature, 32—38°. [b] From iodometric titration. [c] This is also the yield (%) of purified product, except when thiocyanogen was in excess; cf. *d* and *e*. [d] Yield calculated on hydrocarbon, 10%; for the chromatographed product before crystallisation, the yield calculated on hydrocarbon was 56%. [e] Yield calculated on hydrocarbon, 29%.

The overall reaction with arylalkyl hydrocarbons is:

$$Ar{\cdot}CHRR' + (SCN)_2 \longrightarrow Ar{\cdot}CRR'{\cdot}SCN \text{ (or } Ar{\cdot}CRR'{\cdot}NCS) + HSCN$$

Yields of purified products varied from about 10% to 90%, after reaction periods of 0·5—6 hr.; in most cases we employed an excess of the hydrocarbon and continued irradiation

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[5] Bacon, Guy, Irwin, and Robinson, *Proc. Chem. Soc.*, 1959, 304; Bacon, "Thiocyanates, Thiocyanogen, and Related Compounds," in "Organic Sulphur Compounds," Pergamon Press, London, Vol. I, in the press.

[6] Bacon and Irwin, *J.*, 1958, 778.

until the reagent was substantially consumed, as shown by iodometric titration, but we did not ascertain conditions for obtaining optimum yields. There were differences of 10—40% between the total amount of reagent decomposed, determined iodometrically, and the amount which had caused substitution, indicated by yields of purified products. Such differences could be due, in varying degree, to polymerisation of the reagent, to side reactions, and to decomposition of thiocyanation products (see below) or difficulties in their isolation. Chromatography removed resins, but crystalline or liquid products, other than those listed, were not isolated. The reasonably good stability of thiocyanogen when irradiated suggests that polymer-formation accompanying thiocyanation should have been relatively unimportant, but this is uncertain, since little is known about catalysis of the polymerisation, or indeed of its chemical nature. Thiocyanic acid, produced in the thiocyanations, is an additional source of polymer.

We suggest that the substitution involves radical-chain reactions of the type well known for photo-initiated halogenation:

$$(\mathrm{SCN})_2 \xrightarrow{h\nu} 2\cdot\mathrm{SCN} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{Ar{\cdot}CHRR'} + \cdot\mathrm{SCN} \longrightarrow \mathrm{Ar{\cdot}CRR'}\cdot + \mathrm{HSCN} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\mathrm{Ar{\cdot}CRR'}\cdot + (\mathrm{SCN})_2 \longrightarrow \mathrm{Ar{\cdot}CRR'{\cdot}SCN} + \cdot\mathrm{SCN} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

(? or $\mathrm{Ar{\cdot}CRR'{\cdot}NCS}$)

etc.,

followed in some cases by:

$$\mathrm{Ar{\cdot}CRR'{\cdot}SCN} \longrightarrow \mathrm{Ar{\cdot}CRR'{\cdot}NCS} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Step (1) is the homolysis of the disulphide bond of thiocyanogen, giving resonance-stabilised radicals:

$$\mathrm{NCS{-}SCN} \longrightarrow 2(\mathrm{N{\equiv}C{-}S}\cdot \longleftrightarrow \cdot\mathrm{N{=}C{=}S})$$

It has been concluded, from recent studies of S–S bonds in disulphides,[7,8] that their homolysis requires a temperature of about 140°, unless effected by irradiation, or by reaction with other radicals, in which case ordinary temperatures suffice. Evidence given for the photo-initiated homolysis concerns the capacity of the resulting thiyl radicals to cause polymerisation of vinyl compounds and dienes,[9] to accelerate radical-type addition of a thiol to vinyl compounds,[10] and to react with hydrogen-donors and with 1,1-diphenyl-2-picrylhydrazyl.[11] Dialkyl disulphides are not so effective for such purposes as diaryl disulphides, thiuram disulphides, or di(benzothiazol-2-yl) disulphide, all of which produce resonance-stabilised radicals. In thiocyanogen radicals, such stabilisation is due to the constituent cyano-group, in which respect there is a parallel with cyanoalkyl radicals, which are formed readily from azonitriles by heat,[12] or by irradiation from a mercury-vapour lamp:[13]

$$\mathrm{NC{\cdot}CR_2{\cdot}N{:}N{\cdot}CR_2{\cdot}CN} \longrightarrow 2(\cdot\mathrm{CR_2{-}C{\equiv}N} \longleftrightarrow \mathrm{CR_2{=}C{=}N}\cdot) + \mathrm{N_2}$$

Two examples of side-chain thiocyanation of arylalkyl hydrocarbons by thiocyanogen are in the literature. The reaction of 3-methylcholanthrene[14] with thiocyanogen in carbon tetrachloride, presumably influenced by daylight, did not occur in the tetracyclic aromatic ring system, but in a methylene group: $-\mathrm{CH_2{\cdot}CH_2}- \longrightarrow -\mathrm{CH_2{\cdot}CH(SCN)}-$. This

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[7] Moore, *J.*, 1952, 4232.

[8] Bateman, Moore, and Porter, *J.*, 1958, 2866.

[9] Birch, Cullum, and Dean, *J. Inst. Petroleum*, 1953, **39**, 206; Kharasch, Nudenberg, and Meltzer, *J. Org. Chem.*, 1953, **18**, 1233; Otsu, *J. Polymer Sci.*, 1956, **21**, 559.

[10] Rueggeberg, Cook, and Reid, *J. Org. Chem.*, 1948, **13**, 110; Rueggeberg, Chernack, Rose, and Reid, *J. Amer. Chem. Soc.*, 1948, **70**, 2292.

[11] Schaafsma, Bickel, and Kooyman, *Tetrahedron*, 1960, **10**, 76.

[12] Reviewed by Walling, in " Free Radicals in Solution," Wiley and Sons, New York, 1957.

[13] Lewis and Matheson, *J. Amer. Chem. Soc.*, 1949, **71**, 747; Back and Sivertz, *Canad. J. Chem.*, 1954, **32**, 1061.

[14] Wood and Fieser, *J. Amer. Chem. Soc.*, 1941, **63**, 2323.

recalls the influence of daylight in promoting substitution of the methyl group when methylnaphthalenes react with thiocyanogen chloride.[1] A second example,[15] which we repeated (see Table), is the thiocyanation of the isopropyl group in 7-isopropyl-1-methylphenanthrene (retene), but in this case a mercury-vapour lamp was employed.

More numerous in the literature,[3] and strongly suggestive of a radical mechanism, are cases of light-promoted reactions of thiocyanogen with olefins. In a re-examination [5,16] of this aspect of thiocyanation, we find it to be more complicated than has been reported, and highly sensitive to variations in experimental conditions. The reaction with arylalkyl hydrocarbons is apparently less sensitive, but a preliminary examination of experimental variables has shown a solvent effect; acetic acid consistently proved inferior to carbon tetrachloride, and, in a series of thiocyanations carried out with isopropylbenzene, the rate of consumption of the reagent in a series of solvents was: $CCl_4 > CHCl_3 > C_6H_6 > EtBr > Et_2O > PhNO_2 > AcOH$. The trend thus displayed is the reverse of that observed [17] for heterolytic thiocyanation of an aromatic nucleus by thiocyanogen chloride.

Comparison of data in the Table suggests that, as might be expected, ease of replacement of hydrogen is in the order, tertiary > secondary > primary α-carbon atom. In retene it is the isopropyl, not the methyl group, which is thiocyanated. However, precise comparisons are difficult to make, since some of the tertiary and secondary arylalkyl derivatives readily undergo elimination reactions, like those of the corresponding halides. Olefins thus formed from isopropyl-substituted hydrocarbons probably polymerise, but, in the thiocyanation of s-butylbenzene, the resulting 2-isothiocyanato-2-phenylbutane was accompanied by 2-phenylbut-2-ene: $\text{Ph·CMeEt·NCS} \longrightarrow \text{Ph·CMe:CHMe} + \text{HSCN}$. A similar elimination, giving stilbene, occurred spontaneously in the secondary thiocyanato-derivative isolated from bibenzyl: $\text{Ph·CH}_2\text{·CHPh·SCN} \longrightarrow \text{Ph·CH:CHPh} + \text{HSCN}$.

The response of the hydrocarbons to thiocyanation should be governed by the relative ease of hydrogen-abstraction in step (2) of the reaction scheme given above. Isolation of an isothiocyanate instead of a thiocyanate could be due, in step (3), to interaction of the resulting arylalkyl radical with a nitrogen atom of thiocyanogen, instead of with a sulphur atom: $\text{NCS·S·C:N} + \text{·CR}_3 \longrightarrow \text{NCS·} + \text{S:C:N·CR}_3$. Alternatively, the initial product could be a thiocyanate which spontaneously isomerises (step 4). In two cases, the crude product was shown to contain an unstable thiocyanate which underwent complete conversion into an isothiocyanate during isolation. For four other cases, where only an isothiocyanate was observed, an initially formed thiocyanate could reasonably have been expected to isomerise at the temperature of the reaction. The result depends essentially on the structure of the hydrocarbon, as appears in the following summary (thiocyanates isomerising during isolation are shown in parentheses):

(i) Hydrogen replaced on a primary α-carbon atom:
Ph·CH_3, $\text{C}_{10}\text{H}_7\text{·CH}_3 \longrightarrow$ thiocyanate
(ii) Hydrogen replaced on a secondary α-carbon atom:
$\text{Ph·CH}_2\text{Me}$,* $\text{C}_{10}\text{H}_7\text{·CH}_2\text{Me}$,* $\text{Ph·CH}_2\text{Pr}^i$, $\text{Ph·CH}_2\text{·CH}_2\text{Ph} \longrightarrow$ thiocyanate
CH_2Ph_2 ($\longrightarrow$ thiocyanate) $\longrightarrow$ isothiocyanate
(iii) Hydrogen replaced on a tertiary α-carbon atom:
Ph·CHMe_2 ($\longrightarrow$ thiocyanate) $\longrightarrow$ isothiocyanate
Ph·CHMeEt, CHPh_3, $\text{C}_{10}\text{H}_7\text{·CHMe}_2$, $\text{C}_{14}\text{H}_8\text{Me·CHMe}_2 \longrightarrow$ isothiocyanate
(* The derived thiocyanate was previously shown [1] to isomerise at or above 120°.)

Hence, production of an isothiocyanate is aided by (*a*) a secondary carbon atom, or preferably a tertiary carbon atom, at the reaction centre, (*b*) the attachment, at this centre, of aryl groups rather than alkyl groups, (*c*) the attachment, at this centre, of polycyclic

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[15] Frederiksen and Liisberg, *Acta Chem. Scand.*, 1951, **5**, 621.
[16] Bacon and Robinson, unpublished investigations.
[17] Bacon and Guy, *J.*, 1960, 318.

aryl groups (*e.g.*, naphthyl, phenanthryl) rather than phenyl groups. Even the primary group $-CH_2{\cdot}SCN$, when attached to the benzanthracene ring system, is converted into $-CH_2{\cdot}NCS$ at 100°.[14]

The type of product obtained on thiocyanation is readily distinguished, as was shown previously,[1] by chemical methods and by infrared spectroscopy; differences in the absorption bands due to $-SCN$ and $-NCS$ groups have recently been discussed exhaustively.[18] For eight of the hydrocarbons in the Table, essential characterisation had already been carried out when thiocyanogen chloride, which gives the same products as thiocyanogen, was used for homolytic substitution.[1,19] Among these hydrocarbons, isopropylbenzene gives a thiocyanate which isomerises during isolation. When thiocyanation was carried out with thiocyanogen chloride,[19] the product, isolated by distillation, was the isothiocyanate. The product here described was shown by infrared spectroscopy to contain a major proportion of the thiocyanate before distillation. The thiocyanate was also present, though in smaller proportion, in the undistilled product of reaction between diphenylmethyl chloride and ammonium thiocyanate in acetone at room temperature. The crude thiocyanation product gave an unstable thiol with lithium aluminium hydride, while the distilled product gave the readily characterised methylamino-compound when similarly reduced, and it gave an adduct with morpholine. Diphenylmethane and thiocyanogen likewise gave the thiocyanato-derivative, which changed into the isothiocyanate when excess of the hydrocarbon was removed by distillation. The same behaviour has been reported for the product obtained with thiocyanogen chloride.[19] A direct preparation of the isothiocyanate from diphenylmethylamine [20] confirms its constitution.

The case of triphenylmethane also requires comment, since thiocyanogen, like thiocyanogen chloride,[19] gave a product identical with that wrongly described in the literature as triphenylmethyl thiocyanate. From the known influence of structural factors (see above), thiocyanation would be expected to give exclusively triphenylmethyl isothiocyanate, and this in fact had been shown by infrared spectral characteristics.[19] Supporting chemical evidence could also be given, but this is unnecessary, since the structure has recently been discussed by Iliceto and his co-workers,[21] who reached the same conclusion as we did.

Thiocyanation of isobutylbenzene, s-butylbenzene, bibenzyl, and retene had not been carried out with thiocyanogen chloride. The products obtained with thiocyanogen were characterised in the usual way and were compared, in the first three cases, with samples obtained by the customary preparative method, namely, treatment of the corresponding arylalkyl halide with an alkali-metal thiocyanate in an organic solvent. The structure of the halide is the main influence determining whether the product isolated is a thiocyanate, an isothiocyanate, or (*e.g.*, for $Ph{\cdot}CMe_2X$, $CHPh_2X$, $C_{10}H_7{\cdot}CHMeX$) a mixture of the two. If the isothiocyanates obtained by homolytic thiocyanation of the hydrocarbons are due to isomerisation of initially formed thiocyanates, some correspondence with the products of the halide reactions is not surprising; isomerisation is currently attributed to the formation (from R–SCN) and the recombination (giving R–NCS) of carbonium and thiocyanate ions,[21,22] which are likewise involved in S_N1 reactions of secondary and tertiary arylalkyl halides with alkali-metal thiocyanates.

EXPERIMENTAL

Thiocyanation Procedure.—Solutions of thiocyanogen (~0·1M) were prepared from bromine and an excess of lead thiocyanate, as previously described, in "AnalaR" carbon

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[18] Caldow and Thompson, *Spectrochim. Acta*, 1958, **13**, 212; Lieber, Rao, and Ramachandran, *ibid.*, 1959, **13**, 296; Ham and Willis, *ibid.*, 1960, **16**, 279, 393; Svatek, Zahradnik, and Kjaer, *Acta Chem. Scand.*, 1959, **13**, 442.

[19] Bacon and Guy, *J.*, 1961, 2428.

[20] Kaye, Kogon, and Parris, *J. Amer. Chem. Soc.*, 1952, **74**, 403.

[21] Iliceto, Fava, and Mazzuccato, *J. Org. Chem.*, 1960, **25**, 1445.

[22] Iliceto, Fava, and Mazzuccato, *Tetrahedron Letters*, 1960, No. 11, 27; Smith and Emerson, *J. Amer. Chem. Soc.*, 1960, **82**, 3076.

tetrachloride,[23] or in acetic acid which had previously been refluxed with 5% of acetic anhydride for 4 hr.[16] The required amount of hydrocarbon was dissolved in a measured amount of thiocyanogen solution in a Pyrex flask, and the mixture was gently stirred while being irradiated with a 250 w "Mazda" ME/D box-type lamp, set at 8 cm. from the wall of the flask. A water-cooled tube inserted into the flask moderated the effect of thermal radiations and kept the solution at an average temperature of 35°. Consumption of thiocyanogen was measured by iodometric titration of aliquot parts.

At the end of a reaction, precipitated polymeric thiocyanogen was removed by filtration, and unchanged reagent was destroyed by dilution with a large excess of water, in the case of acetic acid solutions, or by shaking with water, in the case of carbon tetrachloride solutions. Crude product was then isolated by ether-extraction or by evaporation, respectively, and was purified by chromatography on silica gel with mixtures of light petroleum and benzene.

Some variations in conditions were examined for the reaction of isopropylbenzene (0·05M) with thiocyanogen (0·10M) in carbon tetrachloride. The distance between the flask and the lamp strongly influenced reaction rate; *e.g.*, at 25 cm. 75 min. were required for 50% decomposition of thiocyanogen at 20°, while at 50 cm. 200 min. were required. Relatively small increases in rate resulted from using a quartz instead of a Pyrex flask, or by using a white-walled box in place of the dark-walled box which normally surrounded the apparatus. The effect of variation in the solvent was tested at 20°, with 25 cm. between the lamp and flask; approximate times for 50% decomposition of the thiocyanogen were then: in carbon tetrachloride, 75 min.; in chloroform, 80 min.; in benzene, 100 min.; in ethyl bromide, 115 min.; in diethyl ether, 120 min.; in nitrobenzene, 40% in 200 min.; in acetic acid (containing 5% of acetic anhydride), 20% in 300 min. These times include variable initial periods of ~5 to ~20 min., during which there was negligible reaction, but the slopes of the approximately straight lines, observed for the time–reagent concentration relationship below 50% followed the same order.

The products referred to in the following paragraphs were obtained under conditions summarised in the Table.

Toluene.—After removal of unchanged reagent and solvent, the products from expts. (i)—(iii) with toluene were purified from resinous contaminants by chromatography with 3 : 2 benzene–light petroleum on silica gel. Recrystallisation of the benzyl thiocyanate from ethanol gave needles, m. p. and mixed m. p. 40°.

Ethylbenzene.—The crude reaction products (i) and (ii) were purified by distillation to give 1′-thiocyanatoethylbenzene, b. p. 137—139°/11 mm., n_D^{25} 1·5615, which gave an infrared absorption spectrum identical with that of the samples previously described.[19] 1′-Isothiocyanatoethylbenzene, prepared for comparison by reaction of styrene with sodium thiocyanate in aqueous sulphuric acid,[24] was a lachrymatory and vesicant liquid, b. p. 86°/0·8 mm., n_D^{25} 1·5770, with a broad, strong infrared absorption band at 2094 cm.$^{-1}$.

Isopropylbenzene.—(*a*) The crude products from the thiocyanation of isopropylbenzene, freed from solvent at <45°, showed a strong sharp peak in the infrared absorption spectrum at 2165 cm.$^{-1}$, due to a major proportion of 2-phenyl-2-thiocyanatopropane, and showed a weak, broad band at ~2080 cm.$^{-1}$, due to a minor proportion of 2-isothiocyanato-2-phenylpropane. Reduction with lithium aluminium hydride [19] of products obtained in this way yielded a liquid thiol (*e.g.*, 66%), with characteristic odour, which decomposed when distillation was attempted. Conversion of the thiol into a 2,4-dinitrophenyl sulphide was unsuccessful; treatment in ethanolic solution with silver nitrate, mercuric chloride, or lead acetate gave precipitates of metal derivatives which were unstable; oxidation by air or iodine gave an impure, colourless, crystalline disulphide.

(*b*) Treatment of 2-chloro-2-phenylpropane with ammonium thiocyanate in acetone [19] was carried out for 1 hr. at room temperature; this sufficed to give a 58% yield of the 1′-isothiocyanate on distillation. After removal of solvent from the crude product at <40°, the infrared absorption spectrum of the residue indicated the presence of a minor proportion of thiocyanate and a major proportion of isothiocyanate. On distillation, the products obtained by methods (*a*) or (*b*) underwent complete conversion into 2-isothiocyanato-2-phenylpropane,[19] b. p. 72°/0·2 mm., n_D^{25} 1·5682, which became yellow and deposited resin when kept. Reduction of the isothiocyanate with lithium aluminium hydride [1] gave 2-*methylamino*-2-*phenylpropane* (63%), b. p. 93°/19 mm. (Found: C, 80·2; H, 10·0; N, 9·8. $C_{10}H_{15}N$ requires C, 80·5; H, 10·1;

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[23] Angus and Bacon, *J.*, 1958, 774.
[24] Luskin, Gantert, and Craig, *J. Amer. Chem. Soc.*, 1956, **78**, 4965.

N, 9·4%). The amine and 1-naphthyl isocyanate gave N-*methyl*-N-(2-*phenyl*-2-*propyl*)-N′-1′-*naphthylurea*, obtained in needles (from ethanol), m. p. 136—137° (Found: C, 79·0; H, 6·45; N, 8·7. $C_{21}H_{22}N_2O$ requires C, 79·3; H, 6·9; N, 8·8%). The isothiocyanate and morpholine reacted immediately in acetone to give N-[N′-(2-*phenyl*-2-*propyl*)*thiocarbamoyl*]*morpholine*, which crystallised from light petroleum in needles, m. p. 145° (Found: C, 63·8; H, 7·1; N,10·35; S, 12·3. $C_{14}H_{20}N_2OS$ requires C, 63·6; H, 7·6; N, 10·6; S, 12·1%).

Isobutylbenzene.—The thiocyanation product, purified by distillation, gave 2-*methyl*-1-*phenyl*-1-*thiocyanatopropane* (70%), b. p. 77°/0·1 mm., which was pleasant in odour and showed a strong, sharp peak at 2159 cm.$^{-1}$ in the infrared absorption spectrum (Found: C, 69·4; H, 7·1; N, 7·35; S, 16·6. $C_{11}H_{13}NS$ requires C, 69·1; H, 6·8; N, 7·3; S, 16·75%). For comparison, 2-methyl-1-phenylpropan-1-ol was treated in benzene with dry hydrogen chloride to give 1-chloro-2-methyl-1-phenylpropane, a pleasant-smelling liquid, b. p. 37°/0·1 mm., and this, without distillation, was kept under reflux for 1 hr., and then at room temperature for 12 hr., with ammonium thiocyanate (6 mol.) in acetone. Distillation yielded unchanged chloro-compound, and then 2-methyl-1-phenyl-1-thiocyanatopropane (24%), b. p. 114°/1·6 mm. Reduction of the thiocyanate with lithium aluminium hydride [19] gave 2-methyl-1-phenylpropane-1-thiol, which failed to form the 2,4-dinitrophenyl sulphide but reacted with a 20% solution of lead acetate in 1 : 1 aqueous ethanol to give the yellow *lead salt*, recrystallising from ethanol as prisms, m. p. 148—150° (Found: C, 45·2; H, 4·6; S, 11·8. $C_{20}H_{26}PbS_2$ requires C, 44·7; H, 4·8; S, 11·9%).

s-Butylbenzene.—Distillation of the crude thiocyanation product gave a little 2-phenylbut-2-ene, b. p. 24—28°/0·07 mm., 186°/1 atm., n_D^{25} 1·5395 (Cram [25] gives b. p. 194°, n_D^{25} 1·5393, for the *cis*-isomer, and b. p. 174°, n_D^{25} 1·5192, for the *trans*-isomer). This was followed by 2-*isothiocyanato*-2-*phenylbutane* (58%), b. p. 82—83°/0·07 mm. (Found: C, 69·4; H, 7·05; N, 7·4; S, 16·5. $C_{11}H_{13}NS$ requires C, 69·1; H, 6·8; N, 7·3; S, 16·75%). The isothiocyanate showed a strong, broad infrared band at 2100 cm.$^{-1}$; it possessed similar instability to 2-isothiocyanato-2-phenylpropane; and it gave a morpholine adduct, N-[N′-(2-*phenyl*-2-*butyl*)-*thiocarbamoyl*]*morpholine*, which crystallised from light petroleum in needles, m. p. 107° (Found: C, 65·1; H, 7·5; N, 9·9; S, 11·2. $C_{15}H_{22}N_2OS$ requires C, 64·8; H, 7·9; N, 10·1; S, 11·5%). For comparison, 2-phenylbutan-2-ol [26] was converted into 2-chloro-2-phenylbutane by treatment in light petroleum with dry hydrogen chloride. Washing with aqueous sodium hydrogen carbonate and removal of solvent under reduced pressure left the chloro-compound as a liquid which readily lost hydrogen chloride if warmed. This was treated with ammonium thiocyanate (3 mol.) in acetone, for 1 hr. at room temperature, and the product, after dilution, ether-extraction, and treatment with sodium hydrogen carbonate, was distilled, yielding 2-phenylbut-2-ene (40%) and 2-isothiocyanato-2-phenylbutane (34%), b. p. 87—88°/0·2 mm., which was identical in properties with the sample described above.

2-*Methyl*-, 2-*Ethyl*-, *and* 2-*Isopropyl-naphthalene*.—The products from the thiocyanations were purified by chromatography, as described for corresponding samples obtained with thiocyanogen chloride.[1] The total weights of purified fractions amounted to 60—70% of the crude products added to the column. There were resinous impurities which resisted elution, particularly in the case of the product from 2-isopropylnaphthalene. As indicated in note (*d*) in the Table, the low yield recorded for the pure product from this hydrocarbon was due to difficulty in inducing crystallisation of the liquid isothiocyanate fractions, which were eluted from the column in substantial amount. 2-Thiocyanatomethylnaphthalene, m. p. and mixed m. p. 101°, 2-1′-thiocyanatoethylnaphthalene, m. p. and mixed m. p. 52·5°, and 2-isothiocyanato-2-2′-naphthylpropane, m. p. and mixed m. p. 46°, were thus obtained. Their structures were checked by infrared spectroscopy.

Bibenzyl.—By chromatography of the crude thiocyanation product on silica gel with 1 : 4 benzene–light petroleum, or by direct distillation of the crude product at the pressure of a mercury diffusion pump, 1,2-*diphenylethyl thiocyanate* was obtained as a colourless liquid, b. p. 127°/4 × 10^{-3} mm., some samples of which solidified, giving prisms, m. p. 35—36·5° after recrystallisation from methanol (Found: C, 75·4; H, 5·3; N, 5·9; S, 13·15. $C_{15}H_{13}NS$ requires C, 75·3; H, 5·4; N, 5·9; S, 13·4%). It showed a strong, sharp peak at 2165 cm.$^{-1}$. Distillation was accompanied by decomposition to polymeric thiocyanic acid and *trans*-stilbene, m. p. 124° after recrystallisation from ethanol. Similar decomposition occurred readily when

[25] Cram, *J. Amer. Chem. Soc.*, 1949, **71**, 3883.
[26] Klages, *Ber.*, 1902, **35**, 3507.

a sample of the thiocyanate was stored at room temperature. A sample thrice distilled under reduced pressure at 160° contained <5% of isothiocyanate, as judged by a weak band at 2080 cm.$^{-1}$.

To obtain the compound by an alternative route, 1,2-diphenylethanol,[27] m. p. 68°, was treated in benzene with dry hydrogen bromide, to give 1,2-diphenylethyl bromide,[28] a liquid which underwent dehydrobromination if heated; solvent was removed at <40°. The bromide was kept for 15 hr. at room temperature, in acetone solution, with ammonium thiocyanate (3 mol.). 1,2-Diphenylethyl thiocyanate was isolated (90%) by dilution with water and ether-extraction, and was purified by brief warming with active charcoal, followed by elution from a column of silica gel with 3 : 17 benzene–light petroleum.

The thiocyanate, prepared by either route, was converted by reaction with lithium aluminium hydride [19] into 1,2-diphenylethanethiol (87%), m. p. 29—31°, b. p. 110°/0·25 mm. (lit., m. p. 41°,[29] b. p. 146—148°/4 mm.[30]) (Found: C, 78·8; H, 6·75; S, 14·6. Calc. for $C_{14}H_{14}S$: C, 78·5; H, 6·55; S, 14·9%). This was converted into 2,4-dinitrophenyl 1,2-diphenylethyl sulphide, obtained from ethanol in yellow plates, m. p. 109° (lit.,[29] 108—109°) (Found: C, 63·3; H, 4·3; N, 7·6; S, 8·6. Calc. for $C_{20}H_{16}N_2O_4S$: C, 63·2; H, 4·2; N, 7·6; S, 8·4%). When equimolecular proportions of 1,2-diphenylethyl thiocyanate and thiocyanogen were irradiated for 90 min. in carbon tetrachloride at 30°, only 0·09 mol. of the reagent was consumed, 92% of the thiocyanate was recovered by chromatography, and no dithiocyanate was detected.

Diphenylmethane.—After removal of solvent from the thiocyanation product at <50°, the residual pale yellow liquid showed a sharp infrared peak at 2160 cm.$^{-1}$, due to thiocyanate, but no band due to isothiocyanate. Removal of excess of diphenylmethane by distillation at 78°/0·08 mm. caused isomerisation, since chromatography of the residue with 1 : 9 benzene–light petroleum gave diphenylmethyl thiocyanate (49%), which crystallised from light petroleum as prisms, m. p. 57° (lit.,[20] 56·5—57·5°), not depressed on admixture with the sample obtained [19] with thiocyanogen chloride. With morpholine it gave N-(*N′-diphenylmethylthiocarbamoyl)morpholine*, which crystallised from ethanol in needles, m. p. 152—153° (Found: C, 69·5; H, 6·2; N, 9·2; S, 10·1. $C_{18}H_{20}N_2OS$ requires C, 69·2; H, 6·4; N, 9·0; S, 10·3%). For comparison, diphenylmethyl bromide, b. p. 136°/1·2 mm., was prepared (80%) by bromination of diphenylmethane [31] and was treated with ammonium thiocyanate (3 mol.) in refluxing acetone for 30 min. Infrared spectroscopic examination of the crude product showed the presence of both thiocyanate and isothiocyanate groups. The mixture was heated at 100° for 2 hr. and treated in light petroleum with morpholine, which yielded the derivative of the isothiocyanate, m. p. and mixed m. p. 152°.

Triphenylmethane.—The crude reaction product showed only the very strong band at 2050 cm.$^{-1}$ in the infrared absorption spectrum, due to isothiocyanate. The recrystallised product, m. p. 138° (lit.,[21] 138—138·5°), was identical with that obtained by using thiocyanogen chloride as the reagent,[19] or by treating triphenylmethyl chloride with ammonium thiocyanate in acetone.

Retene.—Abietic acid (from colophony [32]) was heated with palladium–charcoal [33] to afford retene, m. p. 94—97° after one recrystallisation from ethanol (lit.,[33] 100·5—101°). When solvent was removed from the thiocyanation product at <40°, the crude residue showed a strong broad band at 2055 cm.$^{-1}$ due to the isothiocyanate group, but no peak due to thiocyanate. Recrystallisation from ethanol yielded 2-isothiocyanato-2-1′-methyl-7′-phenanthrylpropane as prisms, m. p. 103—106° (lit.,[15] 107·5—108°) (Found: C, 78·6; H, 5·9; N, 4·85; S, 10·7. Calc. for $C_{19}H_{17}NS$: C, 78·3; H, 5·8; N, 4·8; S, 11·2%). It gave the corresponding thiosemicarbazide with hydrazine, m. p. 186—187° (lit.,[15] 188—189°). Reduction with lithium aluminium hydride gave 2-1′-methyl-2-methylamino-7′-phenanthrylpropane, which was converted by 1-naphthyl isocyanate into N-*methyl*-N-2-(2-1′-*methyl*-7′-*phenanthryl)propyl*-N′-1″-*naphthylurea*, difficult to purify and obtained as prisms, m. p. 196·5—198° (Found: C, 82·4; H, 6·0; N, 7·0. $C_{30}H_{28}N_2O$ requires C, 83·3; H, 6·5; N, 6·5%).

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