

132. A New Method of Preparation of Aryl *iso*Thiocyanates.

By J. N. BAXTER, J. CYMERMAN-CRAIG, M. MOYLE, and R. A. WHITE.

Arylthioureas, when heated in chlorobenzene at 150° for 8—10 hr., undergo fission to give good yields of aryl *iso*thiocyanates containing 1, 2, 3, and 4 aromatic rings. The mechanism of the reaction has been investigated.

METHODS of preparation of aryl *iso*thiocyanates¹ include (a) the use of thiocarbonyl chloride² or its precursor thiocarbonyl tetrachloride (the latter reaction fails with naphthyl compounds³), (b) acid-induced fission of an *NN'*-diarylthiourea, involving the loss of 1 mol. of amine, and (c) decomposition of an ammonium aryldithiocarbamate,⁴ the last method giving low yields for naphthyl and other compounds.⁵

It has now been found⁶ that arylthioureas, when heated in a suitable solvent at 150°, undergo fission into ammonia and the aryl *iso*thiocyanate. No *iso*thiocyanate was obtained on attempted vacuum-distillation of 4-diphenyl- or α -naphthyl-thiourea without a solvent.

9-Phenanthryl- and 1-pyrenyl-thiourea were prepared by Frank and Smith's method;⁷ the methods of de Clermont⁸ and Bertram⁹ failed for the latter substance. *N*-4-Diphenylthiourea was obtainable by either method, or from *N*-4-diphenylammonium thiocyanate. The related *N*-4-diphenyl-*S*-methyl*iso*thiourea, ammonium *N*-4-diphenyldithiocarbamate, and *N*-4-diphenylguanidine were prepared, the last by heating *N*-4-diphenyldiguanide.

When *N*-4-diphenylthiourea was heated in solvents of various b. p.s, chlorobenzene gave optimum yields of *N*-4-diphenyl *iso*thiocyanate; 1 : 2-dichlorobenzene also afforded the desired product, though in smaller yield, while nitrobenzene or 1 : 2 : 4-trichlorobenzene gave no *iso*thiocyanate. *N*-4-Diphenyl *iso*thiocyanate had m. p. 63·5—64·5°, though Desai, Hunter, and Kureishy¹⁰ claim m. p. 119—120°. Brewster and Horner¹¹ claim preparation of this *iso*thiocyanate by 3 hours' boiling of the *NN'*-diaryl thiourea with acetic anhydride. This procedure in our hands gave *NN*-diacetyl-4-aminodiphenyl, m. p. 118·5—119°, and *NN'*-diacetyl-*NN'*-bis-4-diphenylurea, hydrolysed by alkali to 4-acetamidodiphenyl. Reaction of acetic anhydride with the *iso*thiocyanate afforded the same products. Werner¹² reported the action of acetic anhydride on *NN'*-diphenylthiourea to give phenyl *iso*thiocyanate in 96, 37, 7, and 0% yield after 5, 30, 45, and 60 minutes' boiling respectively, but did not identify the product of decomposition. This *iso*thiocyanate is known¹³ to give the *N*-acylaniline and diphenylurea when treated with acetic or formic acid, while benzoic anhydride gives *NN*-dibenzoylaniline.¹⁴ The mechanism of *iso*thiocyanate formation was investigated by using α -naphthylthiourea. The rate of evolution of ammonia at 150°, measured during 6 hr., gave the results shown in the Figure. A plot of $\log_{10} C_A^\circ / (C_A^\circ - C_{NH_3})$ (where C_A° = initial concentration of thiourea and C_{NH_3} = concentration of ammonia at time t) was linear only for 1·5 hr., although the "half-time" of the reaction (65 min.) was independent of the magnitude of C_A° . The possibility of the reaction's occurring in three successive steps (a), (b), and (c), with the intermediate formation of a dithiobiuret, could be dismissed in view of the failure of phenyl *iso*thiocyanate and phenylthiourea to give 1 : 5-diphenyldithiobiuret; only *NN'*-diphenylthiourea was obtained

¹ Review: Schroeder, *Chem. Rev.*, 1955, **55**, 181.

² Dyson and George, *J.*, 1924, 1702.

³ Connolly and Dyson, *J.*, 1935, 679.

⁴ Andreasch, *Monatsh.*, 1906, **27**, 1221; Kaluza, *ibid.*, 1912, **33**, 367.

⁵ Dains, Brewster, and Olander, *Univ. Kansas Sci. Bull.*, 1922, **13**, 3.

⁶ Baxter, Cymerman-Craig, Moyle, and White, *Chem. and Ind.*, 1954, 785.

⁷ Frank and Smith, *Org. Synth.*, 1948, **28**, 89.

⁸ De Clermont, *Ber.*, 1876, **9**, 446.

⁹ Bertram, *Ber.*, 1892, **25**, 48.

¹⁰ Desai, Hunter, and Kureishy, *J.*, 1936, 1668.

¹¹ Brewster and Horner, *Trans. Kansas Acad. Sci.*, 1937, **40**, 101.

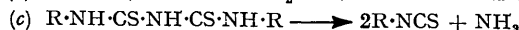
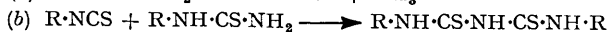
¹² Werner, *J.*, 1891, 396.

¹³ *Idem*, *J.*, 1891, 544; Cain and Cohen, *J.*, 1891, 327.

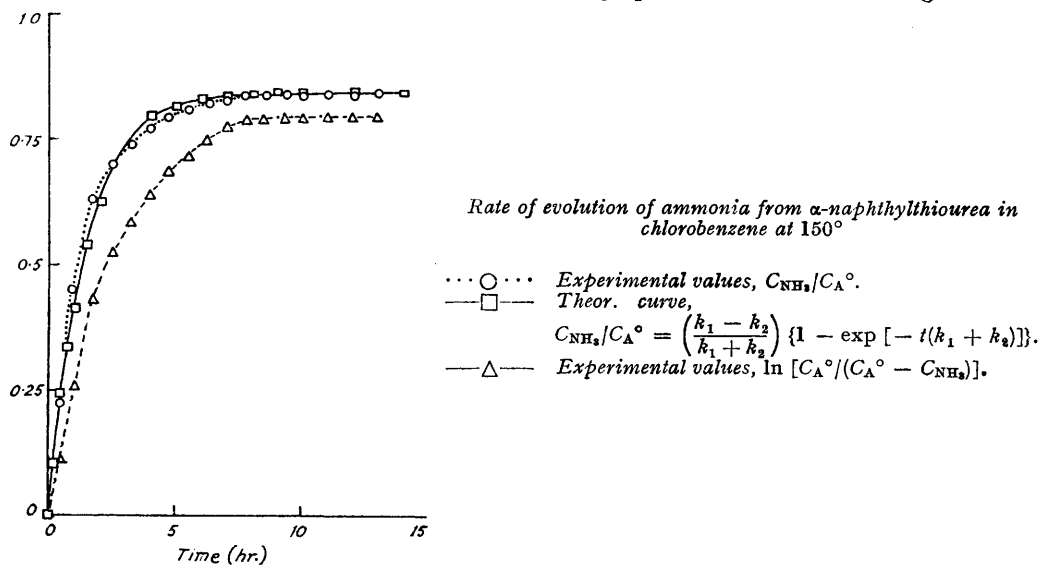
¹⁴ Kay, *Ber.*, 1893, **26**, 2852.

when excess of isothiocyanate was used; equimolar proportions of the reagents did not react even after 7 days at 100°. Curd, Davey, Richardson, and Ashworth¹⁵ have reported abortive attempts to condense aryl isothiocyanates with alkylthioureas, or alkyl isothiocyanates with arylthioureas.

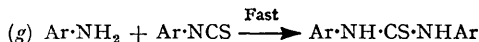
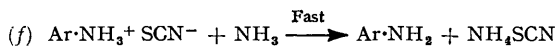
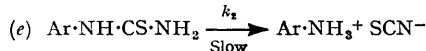
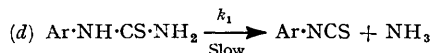
Moreover, 1:5-di- α -naphthylthiobiuret, obtained by thiohydrolysis of 2-methyl-1:5-di- α -naphthyl-2-isodithiobiuret which was prepared by Johnson's method,¹⁶ did not evolve ammonia even after 6 hours' refluxing in chlorobenzene, and was recovered quantitatively.



Investigation of the reaction kinetics for periods up to 14 hr. showed that the evolution of ammonia had virtually ceased after 7 hr. when 85% of the theoretical amount of ammonia had been evolved (see Figure). Working-up after 8 hours' refluxing afforded



the isothiocyanate (86%) and (from a m. p.-composition diagram of the two pure components) a mixture of equal parts of α -naphthylthiourea and di- α -naphthylthiourea. These possess, like most pairs of arylthioureas and diarylthioureas, very similar m. p.s and solubilities, which render their separation difficult. A similar experiment, with working up after 14 hr., gave the isothiocyanate (86%) and pure di- α -naphthylthiourea, while an experiment carried out for the "half-time" of the reaction (65 min.) gave the isothiocyanate (41%), α -naphthylthiourea (53.5%), and a trace of di- α -naphthylthiourea (1.5%).



As these materials together comprised 96% of the expected total, it was clear that no "intermediate compound" was involved. The increasing amounts of the NN' -diarylthiourea and the cessation of the evolution of ammonia could be explained by two

¹⁵ Curd, Davey, Richardson, and Ashworth, *J.*, 1949, 1739.

¹⁶ Johnson, *Amer. Chem. J.*, 1903, 30, 167.

simultaneous first-order reactions (*d*) and (*e*), followed by the known fast reactions (*f*) and (*g*), which would result in the removal of some of the products of reaction (*d*) to form the *NN'*-diarylthiourea. Assuming reactions (*d*) and (*e*) to be rate-determining, and (*f*) and (*g*) to be very fast compared with (*d*) and (*e*), then the following conditions hold :

$$dC_{\text{NH}_3}/dt = (k_1 - k_2)C_A \quad \dots \quad (1)$$

$$-dC_A/dt = (k_1 + k_2)C_A \quad \dots \quad (2)$$

$$C_A = C_A^\circ \exp [-t(k_1 + k_2)] \quad \dots \quad (3)$$

whence

$$dC_{\text{NH}_3}/dt = (k_1 - k_2)C_A^\circ \exp [-t(k_1 + k_2)] \quad \dots \quad (4)$$

and

$$\frac{C_{\text{NH}_3}}{C_A^\circ} = \left(\frac{k_1 - k_2}{k_1 + k_2} \right) \{1 - \exp [-t(k_1 + k_2)]\} \quad \dots \quad (5)$$

When $t = \infty$, from (5) we get :

$$C_{\text{NH}_3}/C_A^\circ = (k_1 - k_2)/(k_1 + k_2) \quad \dots \quad (5a)$$

Further, (5) can be re-written in the form

$$\ln \frac{C_A^\circ - C_{\text{NH}_3}}{C_A^\circ} = \ln \left[1 - \left(\frac{k_1 - k_2}{k_1 + k_2} \right) \{1 - \exp [-t(k_1 + k_2)]\} \right] \quad \dots \quad (6)$$

Expanding the exponential and the logarithmic term, and neglecting terms in t^3 and higher powers of t , we have :

$$\ln [(C_A^\circ - C_{\text{NH}_3})/C_A^\circ] = -t(k_1 - k_2)(1 - k_2t)$$

so that

$$2.303 \log_{10} [C_A^\circ/(C_A^\circ - C_{\text{NH}_3})] = t(k_1 - k_2)(1 - k_2t) \quad \dots \quad (7)$$

When t is very small ($t \ll 1$), then since k_2 is very small (see below), $(1 - k_2t) = ca. 1$ and

$$2.303 \log_{10} [C_A^\circ/(C_A^\circ - C_{\text{NH}_3})] = ca. t(k_1 - k_2) \quad \dots \quad (7a)$$

From the Figure, at $t = \infty$, equation (5a) gives

$$C_{\text{NH}_3}/C_A^\circ = 0.845 = (k_1 - k_2)/(k_1 + k_2) \quad \dots \quad (8)$$

so that $k_1 = 11.90k_2$.

The initial slope of the logarithmic curve in the Figure is constant up to $t = 1$, and, from (7a), slope = $0.25 = (k_1 - k_2)/2.303$, so that

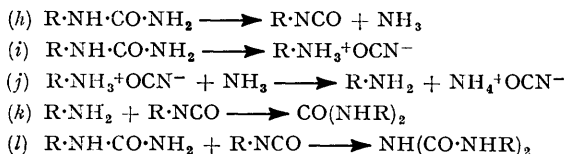
$$k_1 = 0.576 + k_2 \quad \dots \quad (9)$$

From (8) and (9), $k_1 = 0.629 \text{ hr.}^{-1}$ and $k_2 = 0.053 \text{ hr.}^{-1}$. A plot of the theoretical curve (5), with these values of k_1 and k_2 (Figure) is in excellent agreement with the experimental values. Further, a plot of $[C_{\text{NH}_3}/C_A^\circ]_{\text{obs}}$ against $\exp [-t(k_1 + k_2)]$ is linear.

Measurement of the reaction rate in the highly polar benzonitrile gave a greatly reduced rate, only 45% of the theoretical amount of ammonia being evolved after 6.5 hr. From the initial slope of the logarithmic curve for this solvent (0.07), it follows that $k_1' = 0.161 + k_2'$ in this case. No α -naphthyl isothiocyanate could be isolated after 6.5 hr. in this solvent; it is possible that the more polar medium preferentially enhances the reaction (*e*) involving the more polar species. In the less polar chlorobenzene, free ions are less likely to exist, though transitory formation of ion-pairs may occur. The fact that reaction in the non-polar xylene gave 86.5% of the isothiocyanate after 8 hr. is in agreement with this suggestion.

Application of the synthetic method to other arylthioureas showed that 8—10 hours' heating in chlorobenzene at 150° gave good yields of aryl isothiocyanates for systems containing 1, 2, 3, and 4 aromatic rings.

The action of heat on α -naphthylurea in the same solvent gave no α -naphthyl isocyanate, although ammonia was evolved. The residue was a mixture of 1 : 5-di- α -naphthylbiuret (8%) and NN' -di- α -naphthylurea (86%). Probably reactions (h)—(k) ¹⁷ and (l) ¹⁸ occur :



The theoretical increase in the rate of reactions of the more polar CO compounds, compared with their less reactive CS analogues, is shown not only in the increased rates of reactions (i)—(k), but also in the occurrence of reaction (l), which does not take place at all in the CS series. As expected, reactions (i)—(k) are much faster than (l).

EXPERIMENTAL

Kinetic Measurements.— α -Naphthylthiourea (2.02 g., 0.01 mole) was placed in a small 3-necked flask through which was passed a slow stream of dry nitrogen, saturated with chlorobenzene vapour. The gas passed out through a double-surface condenser into a known volume of 0.1N-hydrochloric acid. The temperature was kept at 150° by the use of an oil-bath, and at zero time heated chlorobenzene (40 c.c.) was added to the thiourea. The rate of evolution of ammonia was measured by back-titration of 1 c.c. samples of the acid with 0.02N-barium hydroxide.

Determination of "Half-time."—When 2.02 g. of α -naphthylthiourea were dissolved in 40 c.c. (0.25M-solution), 45 c.c. (0.222M-solution), or 60 c.c. (0.167M-solution) of chlorobenzene, 50% of the theoretical volume of ammonia was evolved after 65 min. in each case.

Preparation of Aryl isothiocyantes.—M. p.s of thioureas were determined at the same time as a mixed m. p. and that of the pure thiourea as standard. Mixtures of thioureas and dithioureas were fractionally crystallised, and where inseparable, were analysed by m. p.-composition diagrams and mixed m. p.s with pure substances and with standard mixtures.

α -Naphthyl isothiocyante. (a) α -Naphthylthiourea (16.16 g.) and chlorobenzene (180 c.c.) were heated under reflux at 150° for 8 hr., and the chlorobenzene distilled off *in vacuo* first at 20 mm. and then at 1 mm. The residue was extracted with hexane (4 \times 30 c.c.), and removal of solvent from the combined extracts gave α -naphthyl isothiocyante (12.75 g., 86%) as needles, m. p. 58—58.5° (lit., 58°). The hexane-insoluble solid (1.3 g.) consisted of α -naphthylthiourea (0.65 g., 4%) and di- α -naphthylthiourea (0.65 g., 5%).

(b) Repetition of the above experiment but with refluxing for 14 hr. gave α -naphthyl isothiocyante (86%) and di- α -naphthylthiourea (1.4 g., 10.5%). No α -naphthylthiourea remained.

(c) Refluxing of α -naphthylthiourea (4.04 g.) and chlorobenzene (40 c.c.) at 150° for 65 min. gave, on cooling to 0°, unchanged α -naphthylthiourea (1.85 g., 46%). Removal of solvent from the combined filtrate and hexane washings, and extraction of the residue with hexane, gave α -naphthyl isothiocyante (1.5 g., 41%) as the hexane-soluble, and a mixture of α -naphthylthiourea (0.3 g., 7.5%) and di- α -naphthylthiourea (0.05 g., 1.5%) as the hexane-insoluble portion.

(d) α -Naphthylthiourea (6.73 g.) and xylene (100 c.c.) were refluxed at 150° for 8 hr., the solvent was removed *in vacuo*, and the residue extracted with hexane. The hexane-soluble portion was α -naphthyl isothiocyante (5.33 g., 86.5%), and the hexane-insoluble fraction weighed 0.1 g.

Phenyl isothiocyante. Phenylthiourea (6.1 g.) and chlorobenzene (60 c.c.) were refluxed at 150° for 8 hr. On cooling to 0°, recovered phenylthiourea separated (1.5 g., 24.5%). Evaporation of the filtrate and hexane washings, extraction of the residue with hexane, and distillation of the extracts gave phenyl isothiocyante (2.37 g., 44%), b. p. 110—112°/20 mm., n_D^{25} 1.6465 (lit., b. p. 95°/12 mm., n_D^{25} 1.6490). The hexane-insoluble fraction was diphenylthiourea (1.2 g., 26%).

o-Chlorophenyl isothiocyante. Refluxing *o*-chlorophenylthiourea (18.65 g.) in chlorobenzene (140 c.c.) at 150° for 8 hr. and working up as described for the phenyl analogue gave unchanged

¹⁷ Cf. Davis and Underwood, *J. Amer. Chem. Soc.*, 1922, **44**, 2595.

¹⁸ Kuhn and Hentschel, *Ber.*, 1888, **21**, 504.

o-chlorophenylthiourea (3.25 g., 17.5%), and *o*-chlorophenyl isothiocyanate (7.9 g., 46.5%), b. p. 91°/1.5 mm., n_D^{25} 1.6604 (Found: C, 49.6; H, 2.35. Calc. for C_7H_4NCIS : C, 49.6; H, 2.3%). Dyson *et al.*¹⁹ give b. p. 260—262°/760 mm. The isothiocyanate, with *o*-chloroaniline at 100° formed di-*o*-chlorophenylthiourea, m. p. 132—133°. The hexane-insoluble portion was di-*o*-chlorophenylthiourea (3.2 g., 23.5%).

N-4-Diphenylthiourea.—(a) Preparation by a modification of Frank and Smith's method⁷ gave *N*-4-diphenylthiourea (92.5%) as plates, m. p. 190.5—191° (from propan-2-ol) (Found: N, 12.15. Calc. for $C_{13}H_{12}N_2S$: N, 12.25%).

(b) A mixture of 4-diphenylammonium chloride and ammonium thiocyanate (5 mols.) in water, after refluxing for 4 hr., gave, on cooling, *N*-4-diphenylthiourea (84.5%), m. p. 190°. With rapid heating, this resolidified and then had m. p. 219° (decomp.) (Found: C, 68.6; H, 5.6; N, 12.05; S, 13.6. Calc. for $C_{13}H_{12}N_2S$: C, 68.4; H, 5.3; N, 12.25; S, 14.0%). Desai *et al.*¹⁰ give m. p. 204°.

4-Diphenylammonium Thiocyanate.—A solution of 4-aminodiphenyl (3.38 g.) in ether (100 c.c.), treated with ethereal thiocyanic acid (from 1.67 g. of ammonium thiocyanate²⁰), gave the thiocyanate (3.8 g., 83%), crystallising from ethyl acetate (with the minimum of heating) as prisms, m. p. 155—156° (bath pre-heated to 155°) (Found: C, 68.7; H, 5.4. $C_{12}H_{11}N,HSCN$ requires C, 68.4; H, 5.3%). It gave a thiocyanate test with ferric chloride and was converted into the thiourea by boiling water in presence of a trace of acid or alkali.

N-4-Diphenyl-S-methylisothiourea.—*N*-4-Diphenylthiourea (2.28 g.), methyl iodide (1.5 g.), and ethanol (20 c.c.), refluxed for 20 min., gave, on cooling, *N*-4-diphenyl-S-methylthiuronium iodide (3.3 g., 89%) as prisms, m. p. 203—205°, unchanged on crystallisation from alcohol-ether (Found: N, 7.65. $C_{14}H_{14}N_2S,HI$ requires N, 7.6%). The base, obtained by using dilute ammonia solution, formed needles, m. p. 161—161.5° (decomp.; bath pre-heated to 150°) (Found: N, 11.75. $C_{14}H_{14}N_2S$ requires N, 11.6%).

Ammonium 4-Diphenylidithiocarbamate.—Ammonia solution (15 c.c.; d 0.880) was added to 4-aminodiphenyl (17 g.) and carbon disulphide (10 c.c.) in alcohol (30 c.c.) with shaking; the mixture was kept at 10° for 3 hr. The solid was washed with ether and recrystallised by refluxing with methanol (100 c.c. per g.) for 1 min., filtering hot, and chilling the filtrate to 0°, giving the ammonium salt (7.8 g., 30%) as pale yellow plates, m. p. 105—106° (decomp.) (Found: N, 10.2. $C_{13}H_{14}N_2S_2$ requires N, 10.6%). Further recrystallisation or heating gave *NN'*-bis-4-diphenylthiourea, m. p. and mixed m. p. 228°.

N-4-Diphenylldiguanide.—Prepared by refluxing a mixture of 4-diphenylammonium chloride (9.86 g.), dicyandiamide (4.4 g., 1.1 mol.), and alcohol (100 c.c.) for 7.5 hr., *N*-4-diphenylldiguanide hydrochloride (9.3 g., 67%) crystallised from aqueous alcohol as prisms, m. p. 236.5—237° (Found: N, 24.1. $C_{14}H_{15}N_5,HCl$ requires N, 24.15%). The benzenesulphonate (m. p. 214—215°) was identical with that reported by Baxter *et al.*²¹

N-4-Diphenylldiguanidine.—*N*-4-Diphenylldiguanide benzenesulphonate (3.9 g.) was heated at 200—210° for 1 hr. Crystallisation from water gave *N*-4-diphenylldiguanidinium benzenesulphonate (1.09 g., 31%), m. p. and mixed m. p. 170—171°.

4-Diphenyl isoThiocyanate.—Reaction of *N*-4-diphenylthiourea (4.56 g.) in chlorobenzene (60 c.c.) at 150° for 6 hr. gave 4-diphenyl isothiocyanate (2.08 g., 49%), crystallising from light petroleum (b. p. 40—60°) as pale yellow needles, m. p. 63.5—64.5°, b. p. 340°/760 mm. (Found: C, 73.85; H, 4.4. Calc. for $C_{13}H_9NS$: C, 73.9; H, 4.2%). Brewster and Horner¹¹ report m. p. 60°, but Desai *et al.*¹⁰ give m. p. 119—120°. The isothiocyanate reacted quantitatively with 4-aminodiphenyl in benzene, to give bis-4-diphenylthiourea, m. p. and mixed m. p. 228—229°.

The hexane-insoluble portion (3.1 g.) consisted of *N*-4-diphenylthiourea (0.33 g., 7%) and bis-4-diphenylthiourea (1.5 g., 39.5%).

Action of Acetic Anhydride on *NN'*-Bis-4-diphenylthiourea.—Acetic anhydride (30 c.c.) and bis-4-diphenylthiourea (7.6 g.) were refluxed for 3 hr., the solvent was removed *in vacuo*, and the residue extracted (Soxhlet) with light petroleum (b. p. 40—60°). Evaporation of the light petroleum extract gave *NN*-diacetyl-4-aminodiphenyl (4.1 g., 82%), crystallising from light petroleum as needles, m. p. 118.5—119° (Found: C, 75.45; H, 5.8. Calc. for $C_{16}H_{15}O_2N$: C, 75.85; H, 5.9%). Scarborough and Waters²² give m. p. 121° (corr.).

Reaction of *NN*-diacetyl-4-aminodiphenyl with 4-aminodiphenyl (1 mol.) in boiling benzene

¹⁹ Dyson, George, and Hunter, *J.*, 1926, 3042.

²⁰ Kaufmann and Kogler, *Ber.*, 1925, 58, 1554.

²¹ Baxter, Cymerman, and Sheldon, *J.*, 1951, 2342.

²² Scarborough and Waters, *J.*, 1927, 1139.

gave 4-acetamidodiphenyl (100%), m. p. and mixed m. p. 169°. Hydrolysis of *NN*-diacetyl-4-aminodiphenyl with 2.5*N*-sodium hydroxide or 2*N*-sulphuric acid gave 4-acetamidodiphenyl (80%), m. p. and mixed m. p. 169°.

The petroleum-insoluble residue from the Soxhlet extraction crystallised from alcohol as plates (4.15 g., 46%) of *NN'*-diacetyl-*NN'*-bis-4-diphenylthiurea, m. p. 148.5—149° [Found: C, 77.95; H, 5.8; N, 6.2; O, 10.8%; *M* (Rast), 435. $C_{28}H_{24}O_3N_2$ requires C, 77.7; H, 5.4; N, 6.25; O, 10.7%; *M*, 448]. Refluxing the urea with 2.5*N*-sodium hydroxide gave 4-acetamidodiphenyl, m. p. and mixed m. p. 169°.

Action of Acetic Anhydride on 4-DiphenylthioisoThiocyanate.—Acetic anhydride (7 c.c.) and 4-diphenylthioisothiocyanate (1.06 g.) were refluxed for 3 hr. Working-up as above gave *NN*-diacetyl-4-aminodiphenyl (0.83 g., 66%), m. p. and mixed m. p. 118—119°, and *NN'*-diacetyl-*NN'*-bis-4-diphenylthiurea (0.3 g., 27%), m. p. and mixed m. p. 147.5—148°.

β-NaphthylthioisoThiocyanate.—Obtained by refluxing *β*-naphthylthiurea (16.2 g.) in chlorobenzene (180 c.c.) for 10 hr. at 150°, *β*-naphthylthioisothiocyanate (10.4 g., 70%) formed yellowish needles, m. p. 61—62° (lit., m. p. 62—63°). The hexane-insoluble portion consisted of *β*-naphthylthiurea (1.08 g., 6.5%) and di-*β*-naphthylthiurea (1.75 g., 13.5%).

p-BromophenylthioisoThiocyanate.—Reaction of *p*-bromophenylthiurea (18.5 g.) in chlorobenzene (200 c.c.) at 150° for 8 hr. gave the isothiocyanate (12.5 g., 73%) as yellow needles, m. p. 60—61° (lit., m. p. 61°). The hexane-insoluble solid was a mixture of *p*-bromophenylthiurea (1.1 g., 6%) and di-*p*-bromophenylthiurea (1.1 g., 7%).

9-PhenanthrylthioisoThiocyanate.—Prepared by an adaptation of Frank and Smith's method,⁷ 9-phenanthrylthiurea (64%) crystallised from propan-2-ol as plates, m. p. 203—204° (decomp.). May²³ gives m. p. 203—204° (decomp.).

9-PhenanthrylthioisoThiocyanate.—Reaction of 9-phenanthrylthiurea (4.65 g.) in chlorobenzene (70 c.c.) at 150° for 10 hr., followed by removal of solvent *in vacuo* and Soxhlet-extraction of the residue with light petroleum (b. p. 60—90°), gave 9-phenanthrylthioisothiocyanate (3.15 g., 73%) as yellow needles, m. p. 102.5—103° (Found: C, 76.3; H, 4.0; N, 5.8. Calc. for $C_{18}H_{13}NS$: C, 76.55; H, 3.85; N, 5.95%). May²³ gives m. p. 103—103.5°. The petroleum-insoluble portion contained 9-phenanthrylthiurea (0.2 g., 4%) and bis-9-phenanthrylthiurea (0.4 g., 10%).

1-PyrenylthioisoThiocyanate.—Prepared by an adaptation of Frank and Smith's method⁷ from 1-aminopyrene, 1-pyrenylthiurea (5.5 g., 80%) crystallised from chlorobenzene as yellow prisms, m. p. 207—207.5° (Found: C, 73.65; H, 4.4. $C_{17}H_{12}N_2S$ requires C, 73.9; H, 4.4%).

1-PyrenylthioisoThiocyanate.—Refluxing 1-pyrenylthiurea (4.1 g.) in chlorobenzene (60 c.c.) for 10 hr. at 150°, followed by removal of solvent and Soxhlet extraction with *n*-hexane, gave 1-pyrenylthioisothiocyanate (2.75 g., 73%), crystallising from chloroform as orange prisms, m. p. 125—125.5° (Found: C, 78.4; H, 3.5. $C_{17}H_{12}NS$ requires C, 78.7; H, 3.5%). The isothiocyanate reacted with 1-aminopyrene in benzene, to give bis-1-pyrenylthiurea, m. p. 217—219° (lit., m. p. 218—219°). The hexane-insoluble portion contained 1-pyrenylthiurea (0.5 g., 12%) and bis-1-pyrenylthiurea (0.5 g., 14%).

Attempted Preparation of 1:5-Diphenyldithiobiuret.—Phenylthiurea (3.12 g., 1 mol.) and phenyl isothiocyanate (10 g., 4 mols.) were heated at 150° for 0.5 hr. The cold mass was extracted with benzene, the extract affording diphenylthiurea (2 g., 44%) as plates (from alcohol), m. p. and mixed m. p. 149—150°. No phenylthiurea or diphenyldithiobiuret was isolated.

Action of Alkali on S-Methyl-N-phenylthiuronium Iodide.—(a) Addition of dilute aqueous ammonia to a solution of *S*-methyl-*N*-phenylthiuronium iodide at 0° gave *S*-methyl-*NN'*-diphenylisothiourea as needles (from alcohol), m. p. 109° (Found: C, 69.35; H, 5.85; N, 11.05. Calc. for $C_{14}H_{14}N_2S$: C, 69.4; H, 5.85; N, 11.5%). Délepine²⁴ gives m. p. 109°. (b) The action of sodium carbonate on the hydriodide at 0° gave the desired *S*-methyl-*N*-phenylisothiourea (96%).

S-Methyl-N-α-naphthylisothiourea.—Refluxing *α*-naphthylthiurea (30.3 g.) and methyl iodide (21.5 g.) in alcohol (750 c.c.) for 20 min. gave, on removal of solvent, *S*-methyl-*N*-*α*-naphthylthiuronium iodide as prisms, m. p. 182—183° (Found: C, 42.2; H, 3.9. $C_{12}H_{12}N_2S, HI$ requires C, 41.9; H, 3.8%). Treatment of this salt with sodium carbonate at 0° gave the isothiourea (75%), crystallising from chloroform-light petroleum (b. p. 60—90°) as prisms, m. p. 88—89° (Found: C, 66.55; H, 5.5. $C_{12}H_{12}N_2S$ requires C, 66.65; H, 5.5%).

²³ May, *J. Org. Chem.*, 1947, **12**, 443.

²⁴ Délepine, *Bull. Soc. chim. France*, 1902, **27**, 807.

2-Methyl-1 : 5-di- α -naphthyl-2-isodithiobiuret.—Reaction of the above isothiurea (20 g.) and α -naphthyl isothiocyanate in dry ether (800 c.c.) at room temperature for 12 hr. gave the *isodithiobiuret* (25 g., 65%), crystallising from chloroform–light petroleum as prisms, m. p. 138–138.5° (Found : C, 68.5; H, 4.75. $C_{23}H_{19}N_3S_2$ requires C, 68.8; H, 4.75%).

1 : 5-Bis- α -naphthyl-dithiobiuret.—A boiling solution of the preceding *isodithiobiuret* (10 g.) and sodium sulphide (10 g.) in alcohol (400 c.c.) and water (20 c.c.) was treated with hydrogen sulphide for 1 hr. Removal of solvent, acidification (acetic acid), and extraction (Soxhlet) of the solid with chloroform gave the *dithiobiuret* (5.2 g., 54%), as needles (from chloroform), m. p. 220–221° (Found : C, 67.9; H, 3.95. $C_{22}H_{17}N_3S_2$ requires C, 68.15; H, 4.4%).

Attempted Preparation of α -Naphthyl isocyanate.— α -Naphthylurea (4.6 g.) and chlorobenzene (40 c.c.) were refluxed for 8 hr. Evolution of ammonia set in at once, but dissolution did not take place. On cooling, the solid was filtered off (3.7 g.) and fractionally crystallised from acetic acid. The most soluble fraction was 1 : 5-di- α -naphthylbiuret (0.34 g., 8%), m. p. 276–278° (lit., m. p. 278–279°). A mixed m. p. with di- α -naphthylurea was depressed by 30°. The remainder was di- α -naphthylurea (86%), m. p. 285–290° (decomp.) [lit., m. p. 284–287° (decomp.)]. The original chlorobenzene filtrate left no residue on evaporation.

ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY OF SYDNEY, N.S.W.

[Received, August 17th, 1955.]