Studies on the Chemistry of 2,3,5,6-Tetrahydro-6-phenylimidazo[2,1-*b*]-thiazole. III. (1). Reaction with Isocyanates and Isothiocyanates

D. C. H. Bigg (2), A. W. Faull and S. R. Purvis*

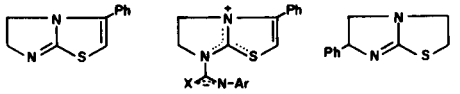
I.C.I. Ltd., Pharmaceuticals Division, Alderley Park, Macclesfield, Cheshire, U.K.

Received March 31, 1977

2,3,5,6-Tetrahydro-6-phenylimidazo[2,1-*b*]thiazole reacts with aryl isothiocyanates to give dipolar 1:1 adducts. The adducts are relatively unstable and, in solution, exist in equilibrium with starting materials. The reaction with aryl and alkyl isocyanates, however, leads to cyclic 2:1 adducts, while sulphonyl and acyl isocyanates give stable dipolar 1:1 adducts.

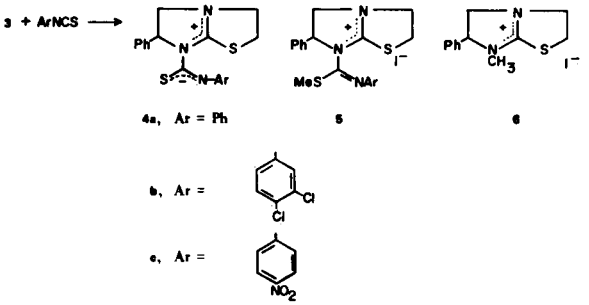
J. Heterocyclic Chem., 14, 989 (1977)

The reactions of cyclic amidines, guanidines and thioureas with isocyanates and isothiocyanates have been extensively studied and generally lead to fused-ring triazines (3), although Ried, *et al.*, have recently reported that the 5,6-dihydroimidazo[2,1-*b*]thiazole **1** gives 1:1 adducts **2** with aryl isothiocyanates and isocyanates (4). We now report the behaviour of 2,3,5,6-tetrahydro-6-phenylimidazo[2,1-*b*]thiazole (**3**) with a variety of isocyanates and isothiocyanates.



1 **2** X = O, S **3**

Aryl isothiocyanates reacted readily with compound **3** to give 1:1 adducts in high yield. The betaines formed (**4**) are much less stable than those derived from compound **1** and, in solution, exist in equilibrium with starting materials. Thus attempted methylation of **4a** in acetone (ϵ: 20.7) led to a mixture of **5** and **6** (1:1), and methylation in acetonitrile (ϵ: 37.5) gave a 4:1 ratio of **5**:**6**.



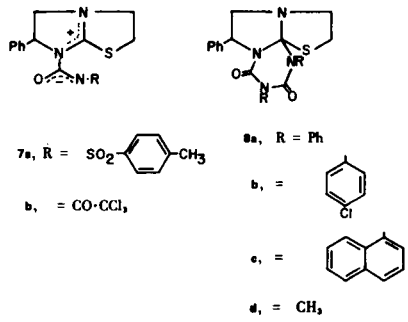
4a, Ar = Ph **5** **6**

4b, Ar =

4c, Ar =

The solution infrared spectra of compounds **4a-c** exhibited strong absorptions in the 2100 cm^{-1} region, characteristic of isothiocyanates, which were absent from spectra registered using nujol mulls. Quantitative infrared spectra on 2% solutions of the betaines **4** showed that the extent of dissociation to starting materials was inversely proportional to the dielectric constant of the solvent. Thus compound **4a** was 98% dissociated in chloroform (ϵ: 4.8), and 87% dissociated in dimethyl sulphoxide (ϵ: 46.7). Electron-withdrawing groups in the isothiocyanatophenyl ring also increased the stability of the betaine, thus the 3,4-dichlorophenyl compound **4b** only dissociates to the extent of 14% in dimethyl sulphoxide, compared to 87% for the unsubstituted compound **4a**.

4-Methylphenylsulphonyl isocyanate and trichloroacetyl isocyanate similarly reacted with **3** to give 1:1 adducts **7** in high yield. In contrast to the zwitterions **4**, compounds **7** did not undergo appreciable dissociation in solution (infrared evidence).



7a, R = SO_2-C_6H_4-CH_3

7b, = CO·CCl,

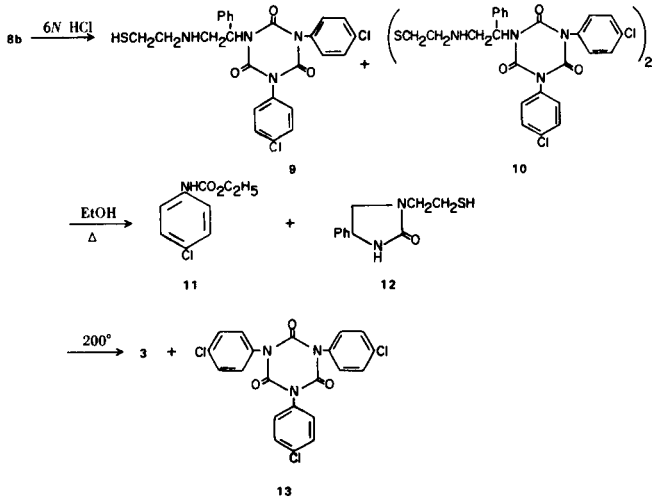
8a, R = Ph

8b, =

8c, =

8d, = CH_3

Aryl or alkyl isocyanates reacted with **3** to give 2:1 adducts **8**. The adducts showed two strong absorption bands in the infrared spectrum in the region of 1700 cm^{-1}, characteristic of carbonyl groups in 1,3,5-triazine-2,4-diones (3b,f), and the assigned structures are consistent with the pmr and mass spectra. Further evidence for the assigned structures was provided by chemical transformations. Thus hydrolysis of **8b**, under acidic conditions, led



9 **10**

11 **12**

13

to the isocyanurate **9** and the corresponding disulphide **10** in an analogous manner to that reported for 1,3-diaryl-8a-pyrrolidinoperhydrothiazolo[3,2-*a*]triazine-2,4-diones (3f). Ethanolysis of **8b** gave the urethane **11** and compound **12**, formed by hydrolysis of **3**, and thermolysis gave the starting imidazo[2,1-*b*]thiazole (**3**) and compound **13**, resulting from trimerisation of the isocyanate.

Compounds **8a-c** appear to be mixed isomers since the signals for the benzylic hydrogen in the pmr spectra are observed as an overlapping triplet and quartet. The carbon-13 spectra also shows almost all signals to be well-resolved doublets. The results are consistent with the existence of geometrical isomers where the phenyl and triazine rings lie on the same, or opposite, sides of the imidazo[2,1-*b*]thiazole ring system. The complexity of the pmr signal is not due to the presence of an asymmetric centre since the 2:1 adduct prepared from the 1-isomer of **3** showed the same coupling pattern for the benzylic hydrogen as the racemic compound.

EXPERIMENTAL

Melting points were determined using a Büchi capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 157 spectrometer using sodium chloride plates. Pmr spectra were recorded at 100 MHz using a Varian HA 100D spectrometer. The chemical shift values are expressed in δ values relative to a tetramethylsilane internal standard. Carbon-13 magnetic resonance spectra (cmr) were determined using a Bruker HX 90E spectrometer with chloroform or tetramethylsilane as an internal standard. The mass spectra were determined on an AE1-MS902 instrument. Microanalyses were carried out on a Carlo Erba Elemental Analyser Model 1104. Column chromatography was performed using silica gel (60-120 mesh) from B. D. H. Ltd.

2,3,5,6-Tetrahydro-6-phenylimidazo[2,1-*b*]thiazolium-7-phenyliminocarbothiolate (**4a**).

Phenyl isothiocyanate (22.6 g., 0.167 mole) was added dropwise to a stirred solution of 2,3,5,6-tetrahydro-6-phenylimidazo[2,1-*b*]thiazole (30.6 g., 0.15 mole) in dry acetonitrile (300 ml.). The white precipitate was collected by filtration after 24 hours at room temperature to give 32.4 g. (64%) of **4a**, m.p. 86-87°. Evaporation of the filtrate left a light yellow solid which was suspended in ether and filtered to give a further 17.3 g. (34%) of **4a**, m.p. 83-85°. Attempts to recrystallise the product from a variety of solvents were unsuccessful; ir (nujol): 1540 cm^{-1} (C=N); pmr (DMSO-d_6): 2.7-3.7 δ (m, 6H), 5.32 (t, 1H, PhCH), 7.3 + 7.4 (s + s, 10H, ArH); mass spectrum: m/e 204 (M-PhNCS), 135 (PhNCS).

Anal. Calcd. for $C_{18}H_{17}N_3S_2$: C, 63.7; H, 5.05; N, 12.4; S, 18.9. Found: C, 63.4; H, 4.9; N, 12.3; S, 19.0.

2,3,5,6-Tetrahydro-6-phenylimidazo[2,1-*b*]thiazolium-7-(3,4-dichlorophenyl)iminocarbothiolate (**4b**).

3,4-Dichlorophenyl isothiocyanate (4.08 g., 0.02 mole) in acetonitrile (5 ml.) was added dropwise to a stirred solution of **3** (4.08 g., 0.02 mole) in acetonitrile (40 ml.). Filtration after 24 hours gave 7.4 g. (91%) of **4b** as a light yellow solid m.p. 140-141°; ir (nujol): 1540 cm^{-1} (C=N); pmr (DMSO-d_6): 3.5 - 3.8 δ (m, 5H, PhCCHN + NCH_2CH_2S), 4.24 (t, 1H, PhCCHN), 6.34 (q, 1H, PhCH), 6.87 + 7.33 (4 line + s, 8H, ArH); mass spectrum: m/e 203, 148 (PhCHNCS), 145.

Anal. Calcd. for $C_{18}H_{15}Cl_2N_3S_2$: C, 52.9; H, 3.70; N, 10.3; S, 15.7. Found: C, 52.9; H, 3.6; N, 10.5; S, 15.5.

2,3,5,6-Tetrahydro-6-phenylimidazo[2,1-*b*]thiazolium-7-(4-nitrophenyl)iminocarbothiolate (**4c**).

A solution of 4-nitrophenyl isothiocyanate (1.8 g., 0.01 mole) in toluene (10 ml.) was added to a solution of **3** (2.04 g., 0.01 mole) in toluene (20 ml.) and the reaction mixture stirred at room temperature for 5 hours. The yellow precipitate was collected by filtration to give 3.5 g. (91%) of **4c**, m.p. 150-152°; pmr (DMSO-d_6): 3.5 - 4.0 δ (m, 5H, PhCCHN + NCH_2CH_2S), 4.30 (t, 1H, PhCCHN), 6.35 (q, 1H, PhCH), 7.35 (s, 5H, C_6H_5), 7.1 + 8.05 (s + s, 4H, $O_2NC_6H_4$).

Anal. Calcd. for $C_{18}H_{16}N_4O_2S_2$: C, 56.2; H, 4.19; N, 14.6; S, 16.7. Found: C, 56.3; H, 4.2; N, 14.4; S, 16.8.

Alkylation of **4a**.

(A) In Acetone.

Iodomethane (5 ml., 0.05 mole) was added to a solution of **4a** (3.4 g., 0.01 mole) in acetone (60 ml.) and the reaction mixture stirred at room temperature for 24 hours. Filtration gave 3.4 g. of a white solid m.p. 133-137°. The melting point was not improved by two recrystallisations from acetone/ether. The pmr spectrum (DMSO-d_6) showed signals at 1.9, 2.9 δ (S-CH_3, NCH_3) corresponding to compounds **5**, **6**, in the ratio 1:1.

Anal. Calcd. for 1:1, **5**:**6**: C, 45.5; H, 4.29; N, 8.42. Found: C, 45.0; H, 4.2; N, 8.2.

(B) In acetonitrile.

Iodomethane (0.7 ml., 0.011 mole) was added to a suspension of **4a** (3.4 g., 0.01 mole) in acetonitrile (50 ml.) and the reaction mixture stirred at room temperature for 24 hours. Filtration gave 4.5 g. of a light yellow solid m.p. 138-141°; pmr (DMSO-d_6): signals at 1.9 and 2.9 δ (S-CH_3, NCH_3) for compound **5**, **6**, ratio 4:1. Two recrystallisations from ethanol/light petroleum b.p. 60-80° afforded 3 g. (62%) of pure **5** (Ar = 3,4-$Cl_2C_6H_3$), m.p. 147-149°; ir (nujol): 1610, 1580 cm^{-1} (C=N); pmr (DMSO-d_6): 1.85 δ (s, 3H, SCH_3), 3.9-4.6 (m, 5H, PhCCHN + NCH_2CH_2S), 5.0 (t, 1H, PhCCHN), 6.45 (q, 1H, PhCH), 6.8-7.7 (m, 10H, ArH).

Anal. Calcd. for $C_{19}H_{20}IN_3S_2$: C, 47.4; H, 4.19; N, 8.73. Found: C, 47.4; H, 4.1; N, 8.6.

Estimation of the Degree of Dissociation of Betaines **4**.

Calibration curves of infrared absorbance for the isothiocyanate group against concentration were established for phenyl- and 3,4-dichlorophenylisothiocyanate solutions (0.5-2.0%) in chloroform and dimethyl sulphoxide. The extent of dissociation of 2% solutions of the adducts to aryl isothiocyanate was determined by comparison of the absorbance of these solutions to the reference curves.

2,3,5,6-Tetrahydro-6-phenylimidazo[2,1-*b*]thiazolium-7-*N*-(4-methylphenylsulphonyl)carbamidate (**7a**).

4-Methylphenylsulphonyl isocyanate (1.97 g., 0.01 mole) was added to a solution of **3** (2.04 g., 0.01 mole) in dry acetone (35 ml.) and the reaction mixture stirred overnight at room temperature. The white precipitate was collected by filtration to give 3.7 g. (92%) of **7a**, m.p. 215-216°; ir (nujol): 1660 cm^{-1} (C=O), 1590 (C=N); pmr (DMSO-d_6): 2.39 δ (s, 3H, $ArCH_3$), 3.3-4.05 (m, 5H, PhCCHN + NCH_2CH_2S), 4.29 (t, 1H, PhCCHN),

5.84 (q, 1H, PhCH), 7.05-7.75 (m, 9H, ArH); mass spectrum: m/e 204 (cpd. **3**), 197 ($ArSO_2NCO$).

Anal. Calcd. for $C_{19}H_{19}N_3O_3S_2$: C, 56.8; H, 4.76; N, 10.5; S, 16.0. Found: C, 56.9; H, 4.7; N, 10.5; S, 16.2.

2,3,5,6-Tetrahydro-6-phenylimidazo[2,1-*b*]thiazolium-7-*N*-trichloroacetylcarbamidate (**7b**).

Trichloroacetyl isocyanate (1.89 g., 0.01 mole) in acetone (10 ml.) was added dropwise with cooling to a solution of **3** (2.04 g., 0.01 mole) in acetone (30 ml.). The reaction mixture was allowed to warm to room temperature after the initial exotherm and stirred for 18 hours. The white crystalline precipitate was collected by filtration to give 3.4 g. (87%) of **7b** m.p. 204-206°; ir (nujol): 1690 cm^{-1} (C=O), 1620 (C=N); pmr (DMSO-d_6): 3.3-4.2 δ (m, 5H, PhCCHN + NCH_2CH_2S), 4.45 (t, 1H, PhCCHN), 6.02 (q, 1H, PhCH), 7.5 (s, 5H, ArH).

Anal. Calcd. for $C_{14}H_{12}Cl_3N_3O_2S$: C, 42.8; H, 3.3; N, 10.7; S, 8.16. Found: C, 43.2; H, 3.1; N, 10.4; S, 8.0.

1,3,6-Triphenylperhydrothiazole[2′,3′:2,3]imidazo[1,2-*a*][1,3,5]-triazine-2,4-dione (**8a**).

Phenylisocyanate (1.19 g., 0.01 mole) was added dropwise to a solution of **3** (2.04 g., 0.01 mole) in dry acetonitrile (20 ml.) and the reaction mixture stirred overnight at room temperature. The precipitate was collected by filtration to give 1.8 g. (82% Calcd. on isocyanate) of **8a** as a fluffy white solid m.p. 178-180°. Recrystallisation of a portion lowered the m.p. to 176-178°; ir (nujol): 1710 and 1670 cm^{-1} (C=O); pmr deuteriochloroform): 2.7-3.0, 3.0-3.48, 3.76 δ (m, m, q, 6H, CH_2N + CH_2S), 5.13, 5.30 (q, t, 1H, PhCH), 7.17-7.6 (m, 15H, ArH); mass spectrum: m/e 442 (M^+) 382 (M-CH_2CH_2S), 381, 263 (382-PhNCO), 262, 119 (PhNCO).

Anal. Calcd. for $C_{25}H_{22}N_4O_2S$: C, 67.9; H, 5.01; N, 12.7; S, 7.2. Found: C, 67.7; H, 5.0; N, 12.6; S, 7.0.

1,3-Di(4-chlorophenyl)-6-phenylperhydrothiazolo[2′,3′:2,3]-imidazo[1,2-*a*][1,3,5]triazine-2,4-dione (**8b**).

4-Chlorophenyl isocyanate (15.4 g., 0.1 mole) was added dropwise to a solution of **3** (10.2 g., 0.05 mole) in dry acetonitrile (100 ml.) and the reaction mixture stirred overnight at room temperature. The precipitate was collected by filtration to give 17.4 g. (68%) of **8b** as a fine white solid m.p. 146-147° (unchanged from toluene/light petroleum b.p. 60-80°); ir (nujol): 1720, 1680 cm^{-1} (C=O); pmr (deuteriochloroform): 2.77-3.14, 3.16-3.55, 3.84 δ (m, m, q, 6H, CH_2N + CH_2S), 5.20, 5.33 (q + t, 1H, PhCH), 7.17-7.62 (m, 13H, ArH); cmr (chloroform): 32.8 ppm, 33.4, 54.1, 54.9, 57.1, 58.3, 61.0, 110.2, 110.9, 125.8, 126.2, 127.5, 127.9, 128.5, 130.3, 131.9, 132.3, 132.6, 132.9, 133.7, 134.5, 138.5, 138.1, 148.0, 148.3, 151.3.

Anal. Calcd. for $C_{25}H_{20}Cl_2N_4O_2S$: C, 58.7; H, 3.94; N, 11.0; S, 6.27. Found: C, 58.4; H, 3.9; N, 11.0; S, 6.2.

1,3-Di(1-naphthyl)-6-phenylperhydrothiazolo[2′,3′:2,3]imidazo-[1,2-*a*][1,3,5]triazine-2,4-dione (**8c**).

1-Naphthylisocyanate (3.4 g., 0.02 mole) was added dropwise to a solution of **3** (2.04 g., 0.01 mole) in dry acetone (35 ml.) and the reaction mixture stirred overnight at room temperature. The white precipitate formed was collected by filtration to give 4.9 g. (90%) of **8c** as a fine solid m.p. 178-179°; ir (nujol): 1710, 1680 cm^{-1} (C=O); pmr (DMSO-d_6): 2.65-3.95 δ (m, 6H, CH_2N+ CH_2S), 5.2-5.85 (m, 1H, PhCH), 7.1-8.55 (m, 19H, ArH); mass spectrum: m/e 542 (M^+), 481 (M-C_2H_5S), 312 (481-ArNCO), 204 (Cpd. **3**), 169 (ArNCO).

Anal. Calcd. for $C_{33}H_{26}N_4O_2S$: C, 73.0; H, 4.83; N, 10.3. Found: C, 72.9; H, 4.7; N, 10.2.

1,3-Dimethyl-6-phenylperhydrothiazolo[2′,3′:2,3]imidazo[1,2-*a*]-[1,3,5]triazine-2,4-dione (**8d**).

Methylisocyanate (1.14 g., 0.02 mole) was added to a solution of **3** (2.04 g., 0.01 mole) in dry acetone (15 ml.) and the reaction mixture stirred at room temperature overnight. Evaporation of the solvent left a viscous yellow oil which crystallised on trituration with light petroleum (b.p. 60-80°) to give 2.9 g. (91%) of **8d** m.p. 139-142° (140-142° from toluene/light petroleum b.p. 80-100°); ir (nujol): 1700, 1670 cm^{-1} (C=O); pmr (deuteriochloroform): 2.95, 3.05, 3.15, 3.3 δ (4 x a, 6H, NCH_3), 2.55-3.6 (m, 5H, PhCCHN + NCH_2CH_2S), 3.88 (t, 1H, PhCCHN), 5.05, 5.25 (q + q, 1H, PhCH), 7.3 (s, 5H, ArH); mass spectrum: m/e 318 (M^+), 258 (M-CH_2CH_2S), 257, 204 (Cpd. **3**), 181.

Anal. Calcd. for $C_{15}H_{18}N_4O_2S$: C, 56.6; H, 5.70; N, 17.6. Found: C, 56.6; H, 5.8; N, 18.0.

Reactions of **8b**.

(A) Hydrolysis.

A suspension of **8b** (5.1 g., 0.01 mole) in a mixture of hydrochloric acid (50 ml. of 6*N*) and acetonitrile (25 ml.) was heated on a steam bath for 5 hours. The reaction mixture was basified with sodium hydroxide (5*N*) and extracted with chloroform (3 x 75 ml.). The combined extracts were dried (magnesium sulfate) and evaporated to give a beige solid which was purified by chromatography through a column of silica gel (400 g.). Elution with acetone gave 0.65 g. (12%) of 1,2-bis(4-chlorophenyl)-3-[*N*-(2-mercaptoethyl)-1-phenyl-2-aminoethyl]perhydro[1,3,5]-triazine-2,4-6-trione (**9**), m.p. 138-140°; ir (nujol): 3250 cm^{-1} (NH), 1690 (C=O); pmr (deuteriochloroform): 1.15 δ (t, 1H, SH), 1.8-2.1 (br., 1H, NH), 2.4-3.05 (m, 4H, NCH_2CH_2S), 3.1-4.1 (m, 2H, $PhCCH_2N$), 6.0 (q, 1H, PhCH), 6.9-7.7 (m, 13H, ArH); mass spectrum: m/e 528 (M^+), 481 (M-CH_2SH), 452 (M-$NHCH_2CH_2SH$), 375 (M-ArNCO), 349 (M-$PhCCH_2NHCH_2CH_2SH$), 153 (ArNCO).

Anal. Calcd. for $C_{25}H_{22}Cl_2N_4O_3S$: C, 56.7; H, 4.19; N, 10.6; S, 6.06. Found: C, 56.6; H, 4.4; N, 10.4; S, 5.8.

Further elution with acetone gave 3.2 g. (61%) of the disulphide **10** as a crystalline white solid, m.p. 84-86°; ir (nujol): 3250 cm^{-1} (NH), 1690 (C=O); pmr (deuteriochloroform + DMSO-d_6): 2.2-3.05 δ (m, 10H, NCH_2CH_2S + NH), 3.1-4.0 (m, 4H, $PhCCH_2N$), 6.0 (q, 2H, PhCH), 7.0-7.6 (m, 26H, ArH).

Anal. Calcd. for $C_{50}H_{42}Cl_4N_8O_6S_2$: C, 56.8; H, 4.00; N, 10.6; S, 6.07. Found: C, 57.2; H, 4.3; N, 10.7; S, 6.2.

(B) Ethanolysis.

A suspension of **8b** (2.56 g., 5 mmoles) in ethanol (50 ml.) was refluxed for 18 hours. Evaporation of the solvent left an oil which was purified by chromatography through a column of silica gel (100 g.). Elution with chloroform gave 1.8 g. (90%) of 4-chlorophenylurethane, m.p. 68-69° [lit. 68° (5)]; ir (nujol): 3250 cm^{-1} (NH), 1700 (C=O); pmr (deuteriochloroform): 1.3 δ (t, 3H, $C-CH_3$), 4.25 (q, 2H, CO_2CH_2-), 6.95-7.5 (m, 5H, ArH).

Anal. Calcd. for $C_9H_{10}ClNO_2$: C, 54.1; H, 5.04; N, 7.02. Found: C, 54.2; H, 5.1; N, 6.9.

Elution with chloroform/ethyl acetate (1/1) gave 0.7 g. (63%) of **12** as a yellow oil: ir (film): 3100 cm^{-1} (NH), 1710 (C=O); pmr (deuteriochloroform): 1.25 δ (t, 1H, SH), 2.8-4.25 (m, 7H, CH_2N + CH_2S + NH), 5.41 (t, 1H, PhCH), 7.04-7.42 (m, 5H, ArH). The spectroscopic data were identical to those of an authentic sample.

(C) Thermolysis.

Compound **8b** (2.0 g.) was heated at 200° under a nitrogen

atmosphere for 1 hour. The glass obtained on cooling was triturated with acetone and ether to give 1.2 g. (100%) of **13** as a white solid, m.p. 313-316° [lit. 315-316° (6)]; ir (nujol): 1690 cm^{-1} (C=O); pmr (DMSO-d_6): 7.55 δ (ArH); mass spectrum: m/e 459 (M^+), 306 (M-ArNCO), 153 (ArNCO).

Anal. Calcd. for $C_{21}H_{12}Cl_3N_3O_3$: C, 54.7; H, 2.62; N, 9.12. Found: C, 54.4; H, 2.7; N, 9.0.

The residue was purified by column chromatography on silica gel. Elution with acetone gave 0.4 g. (50%) of **3**, m.p. and mixed m.p. 86-87°.

1-1,3-Di(1-naphthyl)-6-phenylperhydrothiazolo[2′,3′:2,3]imidazo-[1,2-*a*][1,3,5]triazine-2,4-dione.

1-Naphthyl isocyanate (3.4 g., 0.02 mole) in ethyl acetate (10 ml.) was added dropwise to a solution of 2,3,5,6-tetrahydro-6-phenylimidazo[2,1-*b*]thiazole (2.04 g., 0.01 mole) in ethyl acetate (10 ml.) and the reaction mixture stirred overnight at room temperature. Evaporation of the solvent left a clear oil which solidified on trituration with light petroleum (b.p. 60-80°). Filtration gave 5.2 g. (96%) of the 1:1 adduct m.p. 123-125°; ir (nujol): 1720, 1690 cm^{-1} (C=O); pmr (deuteriochloroform): 2.33-3.34 δ (m, 5H, NCH_2CH_2S + PhCCHN), 3.52 (t, 1H, PhCCHN), 5.0, 5.35 (q + t, 1H, PhCH), 7.0-7.86, 7.96-8.37 (m, 19H, ArH).

Anal. Calcd. for $C_{33}H_{26}N_4O_2S\,1H_2O$: C, 70.7; H, 5.03; N, 10.0; S, 5.72. Found: C, 70.4; H, 4.9; N, 9.6; S, 5.7.

REFERENCES AND NOTES

(1) Part II. D. C. H. Bigg and S. R. Purvis, *J. Heterocyclic Chem.*, in press.

(2) Present address: L.E.R.S., 31 Ave. Paul Vaillant-Couturier, Bagneux, 92220, France.

(3a) H. P. Penner and A. R. Conklin Jr., *J Heterocyclic Chem.*, **4**, 93 (1967); (b) R. Richter, *Chem. Ber.*, **101**, 3002 (1968); (c) R. Richter and H. Ulrich, *ibid.*, **103**, 3525 (1970); (d) C. Di Bello, A. C. Veronese, C. Toniolo, F. Filira and F. D'Angeli, *Gazz. Chim. Ital.*, **100**, 86 (1970); (e) A. C. Veronese, C. Di Bello, F. Filira and F. D'Angeli, *ibid.*, **101**, 569 (1971); (f) D. C. H. Bigg and S. R. Purvis, *J. Heterocyclic Chem.*, **13**, 977, 1119 (1976).

(4) W. Ried, W. Merkel and S. W. Park, *Ann. Chem.*, **79** (1975).

(5) "Dictionary of Organic Compounds", Vol. 2, Eyre and Spottiswoode, Ltd., London, 1965, p. 609.

(6) I. C. Kogon, *J. Am. Chem. Soc.*, **78**, 4911 (1956).